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Background Perchlorate Source Identification Technical Guidance

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EXECUTIVE SUMMARY

The objective of this document is to outline the approach, tools, and methods to quantify and distinguish the relative levels of naturally occurring perchlorate from those derived from anthropogenic sources. This will provide site managers for ranges and facilities with holistic source evaluation and identification of background perchlorate using scientifically defensible forensic approaches and methodologies. This effort brings together the current understanding of natural perchlorate characteristics and behaviors to provide a process for selecting appropriate analytical approaches developed within the environmental forensics community.

The general approach employed in this guidance document is best described by the contaminant source identification (CSI) framework provided in ES-1. This approach was adapted from and is similar to the forensics approach used for pollutant source tracking (PST) of other contaminants (metals, organics, bacteria), for which technical guidance was recently developed under a separate effort (SSC Pacific, 2011).
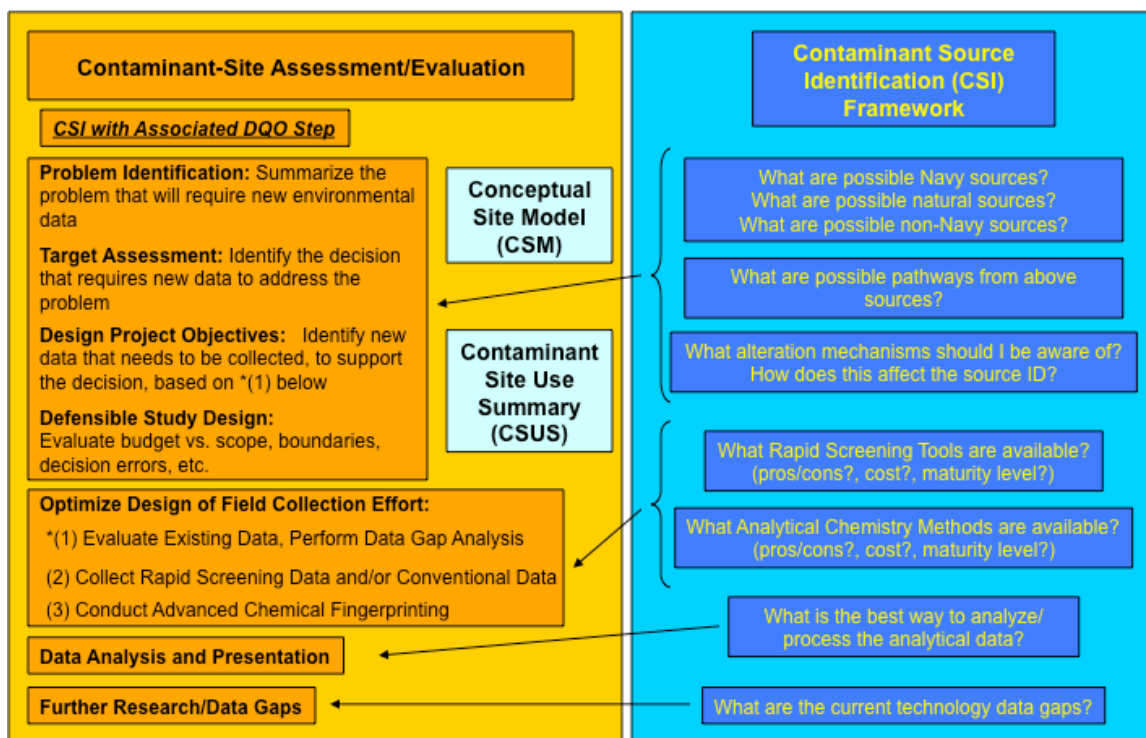

Figure ES-1 Generalized framework for CSI for environmental forensics investigations.

The CSI framework broadly provides the user with the types of forensics questions (right panel of Figure ES-1) that should be addressed, and applies it toward how the forensics analysis should be applied in the context of the CSM and CSUS at a given site for a given contaminant (left panel of Figure ES-1). The forensics questions are addressed in this guidance document to provide the reader with a state of the science assessment for perchlorate. The CSI framework populated for perchlorate is shown in ES-2, and can be used as a roadmap for detailed descriptions of the state of the science assessment in Section 2, and also applied to a case study in Section 4.

Benefit to the Navy

While perchlorate is not federally regulated in the natural environment, it will be facing increased regulatory pressure for future assessments and cleanup. Currently, perchlorate evaluation is part of range condition assessments and monitoring strategies per current Department of Defense (DoD) policy. Range assessments in particular have a direct impact on continued range use for training and testing/operational readiness. Quantifying natural and anthropogenic sources of perchlorate will provide an appropriate baseline for mitigating cleanup efforts and costs (above background levels). Without an understanding of the extent to which background perchlorate sources may be present at or surrounding a site and potentially impacting the site, inaccurate assessments/management decisions will result, ultimately leading to unnecessary cleanup actions at greater expense to the Navy.

Technical Guidance – Perchlorate Source Tracking Framework

Contaminant Source Identification (CSI) Framework

- What are possible Navy sources?
- What are possible non-Navy sources?
- What are possible natural sources?
- What are possible pathways from above sources?
- What alteration mechanisms should I be aware of? How does this affect the source ID?
- What Rapid Screening Tools are available? (pros/cons?, cost?, maturity level?)
- What Analytical Chemistry Methods are available? (pros/cons?, cost?, maturity level?)
- What is the best way to analyze/process the analytical data?
- What are the current technology data gaps?

Solid propellant rockets and missiles, munitions, and explosives (examples in section 4.1.5).

Fireworks, road flares, perchloric cid and reagents manufacture; and chlorate or chlorine manufacture.

Chilean caliche, mineral deposits and atmospheric formation.

High solubility in water can result in increased mobility & transport into environmental matrices.

Biodegradation in groundwater occurs only if significant levels of organic carbon are present, oxygen and nitrate are depleted, and perchlorate-degrading anaerobic bacteria are present.

Ion selective electrode, and colorimetric techniques are inexpensive, but have high limits of detection and suffer interferences by other ions, oils, chlorophyl (See Table 2-3). Surface enhanced Raman methods for field studies now becoming available for plume monitoring/mapping.

Most conventional EPA methods are based on ion chromatography with conductivity detection, but differ in column type and number. Use of liquid chromatography, MS detection, or MS/MS detection with various ionization approaches can help reduce common interferences. (See Table 2-2) Stable isotope analysis (IR-MS) can distinguish natural from synthetic sources, but is expensive, has sample size limitations, and may not allow distinction between different synthetic sources.

Confirm existing data meet adequate DQOs and required LOD. Look for correlations with forensic analytes indicative of source type or with GW dating for contamination timeline. Compare datasets using regression, PCA, other statistical analyses.

More efficient/inexpensive isotopic analyses, improved field sampling/analysis methods, non-traditional forensics correlation analytes may require MDL studies if not typically measured.
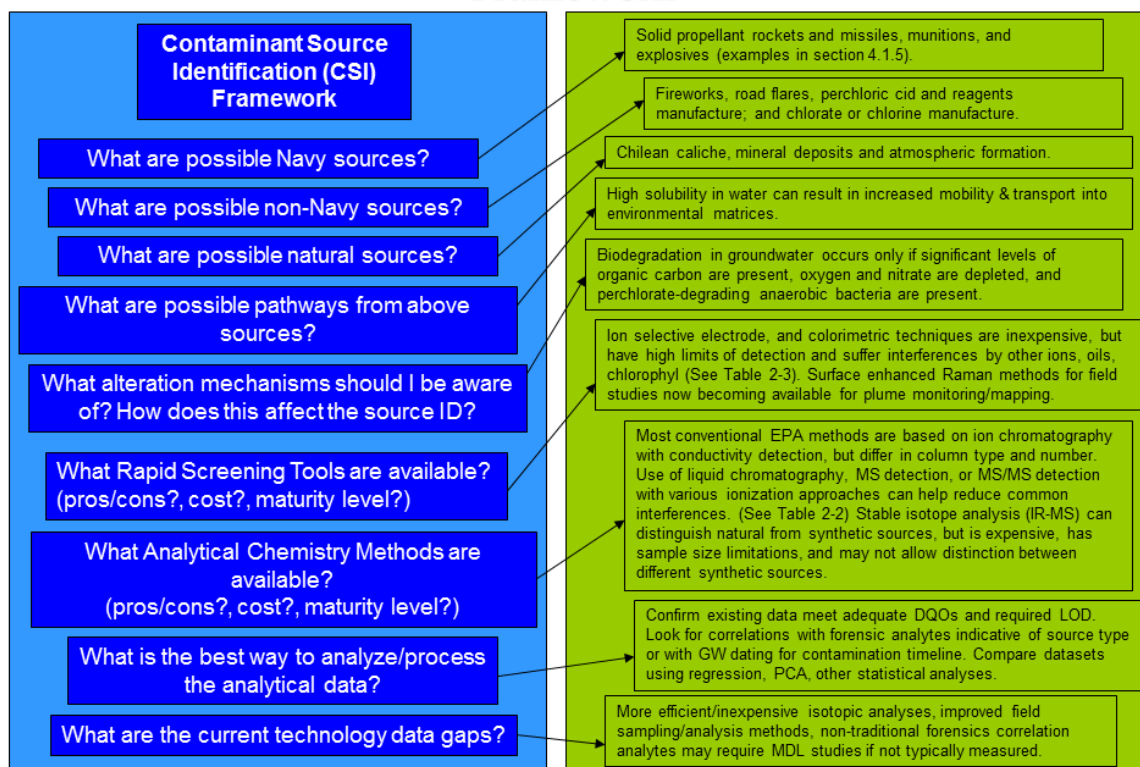
Figure ES-2. CSI framework for perchlorate forensics.

Litigation also continues to be pursued by parties against the Navy as the defendant in such actions. Results of the CSI approach for purposes of source attribution could significantly impact such litigation actions, and reduce Navy liability.

An added aspect may also be realized for scenarios where anthropogenic (synthetic) perchlorate of non-Navy origin is present as part of a background perchlorate signature. Because synthetic sources would be distinguished from natural sources of perchlorate, the potential for a non-Navy source of perchlorate migrating onto a Navy site can also be evaluated, e.g., from an uncontrolled or unregulated source. This could significantly impact environmental risk management decisions, which may be advantageous to the Navy.

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ACRONYMS AND ABBREVIATIONS

A-G	Air-to-Ground
AAF	Army airfield
ATCAA	Air Traffic Control Airspace
B	Boron
Br	Bromine
bgs	Below Ground Surface
C	Carbon
Ca	Calcium
CE	Capillary Electrophoresis
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFC	Chloroflourocarbon
Cl	Chloride
ClO4-	Perchlorate Ion
COE	Corps of Engineers
CSI	Contaminant Source Identification
CSM	Conceptual Site Model
CSUS	Contaminated Site Use Summary
DERP	Defense Environmental Restoration Program
DoD	Department of Defense
DWEL	Drinking Water Effects Level
EFA	Engineering Field Activity
EOD	Explosives Ordnance Disposal
EPA	See USEPA
ESI-MS	Electrospray Ionization - Mass Spectrometry
ESTCP	Environmental Security Technology Certification Program
FDEP	Florida Department of Environmental Protection
FUDS	Formerly Used Defense Site
g	Gram(s)
GCTL	Groundwater Cleanup Target level
GP	General Purpose
GW	Ground Water
H	Hydrogen
HClO4	Perchloric Acid
He	Helium
HMX	Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine
IR	Installation Restoration
IRIS	Integrated Risk Information System
IR-MS	Isotope-Ratio Mass Spectrometry
ITRC	Interstate Technology & Regulatory Council
JATO	Jet-Assisted Take Off
K	Potassium
LC	Liquid Chromatography

LIA	Live Impact Area
MC	Munitions Constituent
MCL	Maximum Contamination Level
mg	Milligram
Mg	Magnesium
mg/kg	Milligram per Kilogram
mg/L	Milligram per Liter
mi	Mile(s)
mm	Millimeter
MOA	Military Operating Area
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MSD	Matrix Spike Duplicate
MW	Monitoring Well
N	Nitrogen
Na	Sodium
NaCl	Sodium Chloride
NAF	Naval Air Facility
NAS	National Academy of Sciences
NAVFAC	Naval Facilities Engineering Command
ND	Non-Detect
Ne	Neon
nmi	Nautical Mile
NO3	Nitrate
NPDWR	National Primary Drinking Water Regulation
NRC	National Research Council
NW	North West
NWSTF	Naval Weapons Systems Training Facility
O	Oxygen
OH	Hydroxide
ORNG	Oregon National Guard
PC	Principal Component
PCA	Principal Components Analysis
PDL	Public Domain Lands
ppb	Parts per Billion
ppm	Parts per Million
PST	Pollutant Source Tracking
PZ	Peizometer
QC	Quality Control
RCA	Range Condition Assessment
RDX	Hexahydro-1,3,5-Trinitro-1,3,5-Triazine
RfD	Reference Dose
RITS	Remediation Innovative Technology Seminar
RSEPA	Range Sustainability Environmental Program Assessment
SCAPS	Site Characterization and Analysis Penetrometer System
SDWA	Safe Drinking Water Act

SERDP	Strategic Environmental Research and Development Program
SERS	Surface Enhanced Raman Spectroscopy
SF	Sulfur Tetrafluoride
SOCAL	Southern California
SOP	Standard Operating Procedure
Sr	Strontium
SSC	Space & Naval Warfare Systems Center
STW	Strike Warfare
SUA	Special Use Airspace
SW	Solid Waste
TCE	Trichloroethylene
TDS	Total Dissolved Solids
TNT	Trinitrotoluene
UFA	Upper Floridan Aquifer
$\mu g/L$	Micrograms per Liter
USDA	United States Department of Agriculture
US EPA	United States Environmental Protection Agency
USGS	United States Geological Service
UV	Ultraviolet
VOC	Volatile Organic Compounds
WD	War Department
RCRA	Resource Conservation and Recovery Act

1. INTRODUCTION

1.1 PERCHLORATE AS A CONTAMINANT

Perchlorate has been the focus of intense scrutiny over the past decade, with contamination largely associated with the manufacture and use of perchlorate salts (e.g., NH_4^+, Na^+, K^+) in various industrial/ aerospace/military applications (U.S. EPA [IRIS], 2005). Anthropogenic perchlorate sources have included such uses as pyrotechnics (fireworks and firecrackers), matches, explosives (black powder and nitric acid), rocket propellants, safety/hazard flares, munitions, airbag inflators, ejection seat propellants, solid rocket propellants, fertilizers, and medical/pharmaceutical uses (potassium perchlorate for thyroid disorders) (Trumpolt et al., 2005). With the exception of the latter two applications/products, perchlorate is generally used as an oxidizer component and as a result, most states have identifiable releases of manufactured (anthropogenic) perchlorate.

Additionally, it has become apparent in recent years that naturally occurring geological sources of perchlorate are present in many areas around the world, but appear to be largely found in arid/semi-arid environments. In contrast to man-made perchlorate sources, geological deposits are primarily evaporites that tend to contribute to environmental concentrations at lower levels, except for the relatively high natural perchlorate concentrations found in Chilean caliche (precipitated salts in soil from evaporated wetting fronts) and some potash ores. Chilean nitrate ore has been brought to the United States for agricultural and explosives usages (Trumpolt et al., 2005).

In environments where both anthropogenic and natural types of perchlorate exist, research to discriminate between the two types has been the subject of much analytical chemistry research (Erickson, 2004). Such efforts have resulted in significant advances in perchlorate analysis that have led to new methods using isotope ratio mass spectrometry (IR-MS) that allow the quantitation and analysis of amounts of ^{37}Cl isotope relative to ^{35}Cl, and amounts of ^{17}O and ^{18}O isotopes relative to ^{16}O in perchlorate samples.

Perchlorate (ClO_4^-) is found in up to four isotopomeric forms which either (1) includes the most common isotopes ^{35}Cl and ^{16}O, (2) includes the rare ^{17}O isotope, (3) includes at least one ^{18}O isotope, or (4) includes isotope ^{37}Cl instead of isotope ^{35}Cl. The general trend in perchlorate samples is that anthropogenic sources are typically "heavier" or enriched with ^{37}Cl (e.g., isotopomer 4) and natural sources are typically "heavier" or enriched with ^{18}O and/or ^{17}O (e.g., isotopomers 2, 3). Also, isotopomer 2 (^{17}O-enriched) is more likely formed atmospherically (mediated by ^{17}O-enriched ozone in the upper atmosphere as described below).

As a result of these observations, for sites that have a significant environmental perchlorate signature with no known history of perchlorate use, isotopic analysis with IR-MS can now be used to clearly identify the isotopic fingerprint or fractions of $^{37}Cl/^{35}Cl$, $^{17}O/^{16}O$, and $^{18}O/^{16}O$ in perchlorate in environmental matrices, thus characterizing perchlorate as naturally occurring or synthetic/anthropogenic in origin. However, while a distinction can be made between synthetic and natural sources, the use of stable isotopes to distinguish between different synthetic/anthropogenic sources of perchlorate is much less definitive.

At another site, in work conducted by Texas Tech University, another very different isotopic ratio signature was reported in areas of the Southwestern U.S. that is indicative of yet another source of perchlorate (Rajagopalan et al., 2006). Increasing observations of perchlorate being detected in areas where it is unexpected, and the observation that perchlorate in groundwater was most strongly correlated with iodate, suggesting atmospheric origin, led to studies that demonstrated it is possible to form perchlorate in a variety of different atmospheric processes. In such scenarios, perchlorate is formed when high levels of ozone are present with UV light activation and/or electrical discharge (lightning), via numerous chemical pathways involving Cl radicals in the atmosphere (Dasgupta et al., 2005). This and the observation that there is widespread occurrence of perchlorate detected at low levels in present day rain and snow samples, strongly supports the likelihood of perchlorate forming in the atmosphere, and the suggestion that a natural perchlorate background of atmospheric origin should exist (Dasgupta, Dyke, Kirk, and Jackson, 2006; Rajagopalan et al., 2006). Atmospheric deposition would lead to a gradual buildup over long time periods

and uptake/bioaccumulation by plants/vegetation. It is also now becoming apparent that perchlorate formation may also occur *in situ* in plants/vegetation, a pathway that appears to be particularly manifested in plants that are ozone-tolerant[1]. Understanding such a pathway is also of interest because it represents a naturally occurring source of potential significance that could be contributing to a broad background perchlorate signature.

1.2 TECHNICAL FOCUS

This effort addresses background perchlorate sources that might impact a Navy range/facility. It incorporates recent advances in the current scientific understanding of background perchlorate formation/characteristics/behaviors in the natural environment and incorporates conventional ion chromatographic (IC) or liquid chromatographic (LC) mass spectrometry (MS) (U.S. EPA Method 332.0 or U.S. EPA Method 331.0, respectively) and newer stable isotopic ratio (IR-MS) methodologies into a perchlorate forensics approach. The impact of background levels of perchlorate at Navy sites is likely broad, as naturally occurring perchlorate has been shown by previous and ongoing scientific studies (e.g., SERDP/ESTCP efforts) to be more prevalent than originally thought. Thus, a significant background level perchlorate signature is probably present in the natural environment, in even the least likely of geographical regions/locales. Such a background pool of natural perchlorate as a source term will significantly impact perchlorate evaluations and subsequent environmental management decisions for Navy ranges and facilities.

1.3 GENERAL APPROACH

The technical effort described herein was focused on the following tasks:

- Providing guidance on forensic analysis methodologies and coordinating with planned or ongoing facility and range assessments to evaluate background perchlorate issues with minimum duplication of effort

- Performing or compiling case studies by leveraging sampling/analysis efforts at sites with strong potential for naturally occurring background levels of perchlorate, and performing supplemental sampling and conventional analysis where necessary

- At select case study sites where the potential for naturally occurring perchlorate represents a significant portion of the total (sum of natural and anthropogenic) perchlorate signature, evaluating the origin or underlying (geological or atmospheric) mechanism of perchlorate formation using targeted sampling combined with advanced analytical and forensics methodologies

Site selection for perchlorate background evaluation can also be based upon regions with high potential for being impacted by an atmospheric deposition pathway and subsequent accumulation into the environment. Because the mechanism of perchlorate formation in the atmosphere or in ozone-tolerant plants relies on ozone as a primary reactant, potential sites with an atmospherically derived perchlorate background are most likely located in ozone nonattainment areas of the United States. (U.S. EPA (Green Book), 2007). An optimal site for distinguishing natural perchlorate from anthropogenic perchlorate can be targeted from evaluating geographical locations with both the presence of perchlorate at a site with no clearly recognized source and a potential pathway for atmospheric formation, as described above for ozone nonattainment areas, to produce perchlorate *in situ* in plants tissues or by perchlorate deposition via precipitation with uptake/bioaccumulation by plants/vegetation through groundwater. A distinct perchlorate signature might also be observed for regions that have geological deposits of perchlorate contributing to background levels. Natural sources are characterized as part of a perchlorate background evaluation and would thus be distinguished from anthropogenic perchlorate. Data collected from soils, groundwater, or plants/vegetation, can also be coordinated with similar data collected for evaluations being conducted at other sites to better understand sources of natural perchlorate. This will ultimately help guide efforts in establishing background levels at Navy sites to assist in risk assessment and/or clean up and remediation decisions.

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[1] Personal communication with G. Harvey, Wright-Patterson Air Force Base, March, 2008.

For sites that have potential for complementary focused sampling and analysis efforts, preliminary samples of plant vegetation, groundwater, or soil could be collected based on site-specific information in regions surrounding a Navy site. The objective of a preliminary sampling event is to initially evaluate total perchlorate background concentrations with conventional analyses. If background samples near a site exhibit levels of perchlorate that have potential for contributing significantly to the total levels of perchlorate at the site, the site can then be evaluated for benefits of a forensic analysis approach, including the use of stable isotope analysis using IR-MS. Appropriate quantities of additional samples would be targeted and collected from those sites (amounts would be dictated by the perchlorate concentration found in the preliminary samples analyzed by conventional analytics). Qualified government or contract analytical laboratories can initially perform the conventional analytics, whereas stable isotope analysis, if feasible, can be leveraged against collaborative efforts with analytical laboratories at other DoD sites. Using this approach, anthropogenic (synthetic) perchlorate is distinguishable from a naturally occurring (atmospherically, or geologically derived) perchlorate background.

2. PERCHLORATE SOURCE TRACKING FRAMEWORK

2.1 BACKGROUND

Perchlorates are highly soluble compounds that dissolve and move like many other ionic salts (e.g., NaCl) in water. Anthropogenic perchlorate is a soluble anion commonly associated with the solid salts of ammonium, potassium, and sodium. Ammonium perchlorate is the mostly widely used perchlorate compound and has also been found to occur naturally in certain highly arid environments. Since these salts are highly soluble in water, and perchlorate adheres poorly to mineral surfaces and organic material, it can be very mobile in surface and subsurface aqueous systems. Also, because it is relatively inert in typical groundwater and surface water conditions, perchlorate contamination may persist for extended periods of time. Because of its high mobility, perchlorate can be transported readily through groundwater and into drinking water supplies, where it is a human health concern due to its similarity in molecular size to the iodide ion. The toxicological mode of action is to interfere with iodine uptake by the thyroid, which results in reduction in thyroid hormone production. This deficiency results in abnormal metabolism, growth and development. It is interesting to note that perchlorate was at one time used to treat thyroid dysfunction, particularly a hyperthyroidism condition known as Grave's disease. Ecological impacts are only slowly being studied, with little known of food chain pathways and effects on higher trophic levels. One particular focus is perchlorate effects on agriculture, i.e., the effects of using perchlorate-contaminated water for irrigation purposes.

Perchlorate is an environmental contaminant found in many areas of the United States, predominantly in water and soil/sediment matrices. Most naturally occurring sources of perchlorate appear to be geographically limited to arid environments. These deposits tend to be of low concentration, except for the relatively high natural perchlorate concentrations found in Chilean caliche (precipitated salts in soil from evaporated wetting fronts) and some potash ores. Chilean nitrate ore has been brought to the United States for several agricultural and explosives uses (Trumpolt et al., 2005). In contrast, man-made perchlorate sources can be many times more concentrated than most natural sources. Man-made perchlorate sources have included pyrotechnics (fireworks and firecrackers), matches, explosives (black powder and nitric acid), rocket propellants, medicine, safety/hazard flares, munitions, airbag inflators, ejection seat propellants, solid fuels, fertilizers, medical/pharmaceutical uses (potassium perchlorate for thyroid disorders), etc. (Trumpolt et al., 2005). It is generally used as an oxidizer component in many of these types of products. Most states have perchlorate users and/or manufacturers; and many have identifiable releases of perchlorate. In environments where both synthetic and natural perchlorate types exist, research to discriminate between them is ongoing (Erickson, 2004).

2.2 REGULATORY STATUS

As of the date of this document, perchlorate is not a federally regulated chemical. The current (2006) EPA regulatory policy is a provisional reference dose (RfD) of 0.0007 mg/kg-day, which leads to a drinking water equivalent level (DWEL) of 24.5 µg/L (ppb). EPA calculates the DWEL using the RfD, multiplied by an adult body weight of 70 kg, and divided by a conservative tap water consumption value of 2 L/day.

Appreciation of widespread contamination in the United States emerged in Spring 1997 when development of an analytical method with a quantitation level at 4 ppb became available. By May of that same year, EPA was engaged in developing a targeted testing strategy to evaluate the potential human health and ecotoxicological effects of potential perchlorate exposures. The National Center for Environmental Assessment first released an external review draft in 1998 and recommendations for additional studies and analyses were made at a 1999 scientific peer review. In 2002, the EPA released a human health risk assessment entitled "Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization (2002 External Review Draft)." In January 2005, the National Research Council (NRC) of the National Academy of Science (NAS) published the results of its review of perchlorate toxicity in a report titled "Health Implications of Perchlorate Ingestion." The NRC reviewed the adverse health effects of perchlorate ingestion from clinical, toxicological, and public health perspectives as well as EPA's 2002 draft

toxicity assessment for perchlorate. The NRC found that daily ingestion of up to 0.0007 mg of perchlorate per kg of body weight can occur without adversely affecting the health of the most sensitive populations. The committee that wrote the NRC report did not include a corresponding drinking water concentration with its RfD because the assumptions used to derive drinking water standards involves public policy choices that were beyond the committee's charge. On 18 February 2005, EPA adopted the findings of the NRC and established an official RfD of 0.0007 mg/kg/day of perchlorate in the Integrated Risk Information System (IRIS). This RfD equates to a drinking DWEL of 24.5 µg/L (EPA IRIS, 2005).

At this time, no federal cleanup standard exists for perchlorate in groundwater or soil, such as a maximum contaminant level (or MCL, an enforceable drinking water standard under the Safe Drinking Water Act [SDWA]). Rather, cleanup levels have been identified on a site-specific basis under federal statutes such as the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA), and the SDWA. In addition, several states have identified advisory levels for perchlorate, as shown in Table 2-1.

A decision was made to not set a MCL in October 2008. In August 2009, the U.S. EPA decided to re-evaluate the toxicology of perchlorate, and reconsider a Federal MCL. The EPA has determined that perchlorate meets SDWA's three criteria for regulating a contaminant: (1) perchlorate may have adverse health effects because scientific research indicates that perchlorate can disrupt the thyroid's ability to produce hormones needed for normal growth and development, (2) there is a substantial likelihood that perchlorate occurs with frequency at levels of health concern in public water systems because monitoring data show over four percent of public water systems have detected perchlorate, and (3) there is a meaningful opportunity for health risk reduction for the between 5.2 and 16.6 million people who may be served drinking water containing perchlorate.

On February 11, 2011, the U.S. EPA announced that the agency would regulate perchlorate under the SDWA. This decision reverses the 2008 preliminary determination, and considers input from almost 39,000 public commenters on multiple public notices (May 2007, October 2008, and August 2009) related to perchlorate. Once the U.S. EPA makes a final determination to regulate a contaminant in drinking water, SDWA requires that the agency issue a proposed national primary drinking water regulation (NPDWR). The proposed NPDWR was issued within 24 months of the February 2011 announcement, and a final NPDWR issuance was expected within 18 months of the proposal. The process will include receiving input from key stakeholders as well as submitting any formal rule to a public comment process (EPA Unregulated Drinking Water Contaminants Website). The publication of the proposed rule for public review and comment was expected in 2013, but as of the date of the publication of this document, no final rule had been issued (see http://water.epa.gov/drink/contaminants/unregulated/perchlorate.cfm for updates).

2.3 PERCHLORATE CHEMISTRY, HISTORY OF USE, RELEASE AND ALTERATION IN THE ENVIRONMENT

2.3.1 Chemical Nature of Perchlorate

Perchlorate is a highly oxidized chlorine-containing anion found in solution, generally derived from solid sodium perchlorate, potassium perchlorate, or ammonium perchlorate salts. The perchlorate ion (Figure 2-1) possesses an ionic charge of -1, is polarizable, nonvolatile, highly soluble in water, and very stable. Perchlorate cannot be removed effectively from water by common filtration, sedimentation, air-stripping, or sorption onto activated carbon. Ion-exchange and biological degradation are the most commonly used approaches to perchlorate removal. Several commercial ion exchange resins suitable for perchlorate have been developed with utility for both analytical chemistry and remedial efforts (Pontius, 2002).
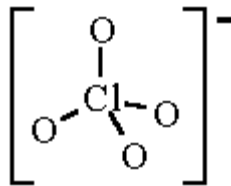
Figure 2-1. Perchlorate Ion.

Perchlorate is a mobile ion that dissolves and moves like other highly soluble ions in water. The four most common perchlorate compounds are ammonium perchlorate, sodium perchlorate, potassium perchlorate and perchloric acid ($HClO_4$).

Table 2-1. Select state perchlorate advisory levels as of 9/26/2012.

http://www.clu-in.org/contaminantfocus/default.focus/sec/perchlorate/cat/policy_and_guidance/		
Alabama	24.5 ppb	Advisory level
Alaska	26 ppb	Advisory level
Arizona	14 ppb	1998 health-based guidance based on child exposures
California	6 ppb	Public health goal
Florida	4 ppb	Advisory level
Hawaii	26 ppb (drinking water) 600 ppb (non-drinking water)	Advisory level
Iowa	4.9 ppb	Advisory level
Kansas	10.9 & 70.9	10.9 ppb= Residential protective cleanup level (PCL) 70.9 ppb= Industrial/Commercial protective cleanup level (PCL)
Maryland	1 ppb (drinking water) 2.6 ppb (groundwater)	Advisory level
Massachusetts	1 ppb (groundwater)	Advisory level for children & other at risk populations for the town of Bourne
Missouri	10.9 ppb	Advisory level
Nebraska	0.91 ppb	Advisory level
Nevada	18 ppb	Public notice standard
New Jersey	5 ppb	Draft MCL (pending)
New Mexico	1 ppb	Drinking water planning level
New York	5 & 18 ppb	5 ppb = Drinking water planning level 18 ppb = Public notification level
North Carolina	2 ppb	Advisory level
Texas	17 & 51 ppb	17 ppb = Residential protective cleanup level (PCL) 51 ppb = Industrial/Commercial protective cleanup level (PCL)
Vermont	4 ppb	Enforceable level
Virginia	15 ppb	Advisory level
Washington	11 ppb	Advisory level
Wisconsin	0.1 ppb	Enforceable level

Perchlorate can be reduced by air-sensitive metal cations, such as titanium(III) or ruthenium(II). It has a low charge density and does not generally form complexes with metals the way other anions do. Most perchlorate salts are quite soluble and do not sorb well to most surfaces (Urbansky, 2002).

2.3.2 History of Perchlorate in the Environment

2.3.2.1 Natural Sources of Perchlorate

The three main natural perchlorate sources are Chilean caliche, mineral deposits, and atmospheric formation (GeoSyntec Consultants, 2005). These are described briefly below.

Chilean caliche

Until recently, naturally occurring perchlorate was known to exist in the environment at only one location - the Atacama Desert in Chile. Similar but less extensive deposits have also recently been found in Peru and Bolivia. The perchlorate in Chile exists in mineralogical association with nitrate of soda caliche deposits that may have been derived in part from past local volcanic activity (Ericksen, 1983; Schumacher, 1960). Chilean nitrate deposits have been mined to produce fertilizer and saltpeter for gunpowder for export since the 1830s. Import of this Chilean nitrate ore into the United States began sometime in the late 1800s for these purposes, in addition to use as a feedstock for making nitric acid, explosives, fireworks, and additional end products.

Chilean nitrate fertilizers have been used widely for various crops, including cotton, tobacco, and fruit trees. Data from Howard (1931), indicate that in 1928 Chilean nitrate accounted for approximately 35% of the total nitrogen fertilizer used that year on a nitrogen basis. It is estimated that an application of 30 to 36 million pounds of Chilean nitrate was added to agricultural oil crops in the 1909 to 1929 timeframe in the states of Georgia, Alabama, South Carolina, and North Carolina (Mehring, 1943). The Chilean application rate for tobacco crops equates to a perchlorate application rate of approximately 0.4 to 0.5 pounds per acre (Bennett, Hawks, and Nau, 1953). It is estimated that 1.2 million pounds of perchlorate have been applied to fruit trees in California from 1923 to 1960 (Collings, 1950).

Mineral Deposits

Evaporite deposits are those formed by evaporation concentration in arid environments. These marine and non-marine deposits include salts of bromine, boron and borates, gypsum and anhydrite, nitrogen compounds, potash, iodine, sodium sulfate, and sedimentary phosphate (Lefond, 1975). Evaporites tend to be deposited in a specific chemical sequence during the salt concentration process, such that potassium or other salts that precipitate after halite (rock salt or sodium chloride) are those most likely to contain perchlorate, based on current sample analysis.

In an initial round of United States Geological Service (USGS) testing, more than 90% of the natural materials samples had detectable perchlorate, some at low concentrations and others involving potash (sylvite) deposits with perchlorate values up to 489 ppm (Orris, Harvey, Tsui, and Eldrige, 2003; Orris, 2004). Potash is mined and milled in the United States, Canada, and elsewhere.

Other evaporite deposits besides potash may also have the potential of associated perchlorate. Some examples include trona, borax, gypsum, Epsom salts, and others. Borates have been used for boric acid production as a pesticide/lumber preservative, and as an ointment. Borax is also used as part of an abrasive hand cleaner. Colemanite is used as a component for some fertilizers for alfalfa and clover (Lefond, 1975).

Atmospheric Formation

While the exact mechanism for the creation of perchlorate is unknown, the general theory is that chloride, possibly in the form of sodium chloride from the sea or land-based chloride compounds blown in from the atmosphere, reacts with atmospheric ozone to create perchlorate. This process probably occurs over much of the earth and is analogous to nitrate formation in the atmosphere (Walvoord et al., 2003). The presence of perchlorate in rain and snow samples shows that it is formed in the atmosphere. Other researchers (Dasgupta et al., 2005) have analyzed how $HClO_4$ is an important sink for stratospheric chlorine. Chlorate radical may be formed as an intermediate that may then be acted on by OH to produce stable $HClO_4$.

The series of underlying atmospheric reactions is

$$Cl\bullet + O_3 + M \rightarrow ClO_3\bullet + M$$
$$Cl\bullet + O_2 + M \rightarrow ClO_2$$
$$Cl\bullet + O_3 \rightarrow ClO_2 + \bullet O$$
$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$
$$ClO\bullet + \bullet O + M \rightarrow ClO_2$$
$$ClO\bullet + O_2 \rightarrow ClO_2 + \bullet O$$
$$ClO\bullet + O_3 + M \rightarrow ClO_2 + O_2$$
$$ClO\bullet + ClO\bullet + M \rightarrow Cl_2O_2$$
$$Cl_2O_2 \rightarrow Cl\bullet + ClO_2$$
$$ClO\bullet + O_2 + M \rightarrow ClO_3\bullet$$
$$Cl_2O_2 + O_3 \rightarrow ClO_3\bullet + ClO_2.$$
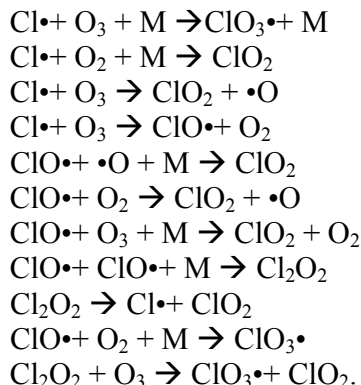
In these series of equations, the ($\bullet$) indicates a radical species, and M indicates mediation by a random air molecule (N_2 or O_2). In addition, it is likely that lightning plays a role in the creation of some atmospherically produced perchlorate, formed from chloride aerosol by electrical discharge as indicated in laboratory studies (Dasgupta et al., 2005; Jackson et al., 2003), but this theory has not been confirmed. Perchlorate can also be formed by exposing aqueous chloride to high concentrations of ozone (Dasgupta et al., 2005). Following atmospheric creation, perchlorate returns to the earth's surface depositionally via precipitation. In arid environments, where this rate of deposition exceeds the rate of dissolution and transport by ongoing precipitation, perchlorate can be incorporated into certain geologic formations (Orris, 2004). Corresponding preliminary analytical results have shown that perchlorate appears to be naturally present in arid environments and appears to concentrate in a manner similar to that of nitrate (Walvoord et al., 2003).

Other Natural Sources

Perchlorate has been detected in seaweed at a concentration of 885 ppm in a sample of kelp collected and analyzed by the USGS (Orris et al., 2003). Bioconcentration of perchlorate and iodide in several types of seaweed has also been studied (Martinelango, Tian, and Dasgupta, 2006). While most seaweed samples were found to contain some perchlorate, it was typically present with iodide in a much greater amount, which resulted in a net nutritional benefit. In these studies, reported seawater concentrations ranged from below 0.07 μg/L (the limit of detection) to 0.345 μg/L for coastal seawater samples collected from the Pacific Ocean (Hawaii, U.S., and the west coast of Mexico), the Gulf of Mexico, and the Atlantic Ocean.

2.3.2.2 Non-Navy Sources of Synthetic Perchlorate

The major non-military anthropogenic sources of perchlorate are fireworks, road flares, perchloric acid and reagents manufacture, and chlorate or chlorine manufacture (GeoSyntec Consultants, 2005). Descriptions of these sources follow.

Fireworks

Perchlorate is a major component of fireworks and is used primarily as an oxidizing agent. Potassium perchlorate can be used to produce purple and yellow colored flames, flashes, sound, whistle noises, and white lights, white sparks, and black smoke in fireworks. Ammonium perchlorate is used in some firework formulations to create red torches and blue flames (Conkling, 1985). Although perchlorate is widely used as an oxidizer in fireworks formulation, information about the amount of perchlorate residue remaining after burning or fireworks is limited (GeoSyntec Consultants, 2005).

Road/Safety Flares

Perchlorate in the form of potassium perchlorate is used in safety/road flares as the burn mixture component of the flare. An unburned, damaged 20-minute road flare can leach 3.6 g of perchlorate and fully burned flares can leach 1.9 mg of perchlorate per flare (Silva, 2003). It is estimated that up to 237,600 pounds of perchlorate could leach from road flares annually (GeoSyntec Consultants, 2005).

Matches

Safety matches and common stick matches use a blend of potassium chlorate and sulfur with a fuel and binder (Conkling, 1990).

Electrochemically-produced Chlorine Products

During the electrochemical manufacturer of chlorine products, small amounts of perchlorate may be formed as an impurity (Wanngard, 1991; Betts and Dluzniewski, 1997). Such chlorates are used for pulp and paper bleaching, non-selective contact herbicide application, and plant defoliation for cotton, sunflowers, safflower, rice, and chili peppers (OMRI, 2000). Effluents from pulp mills have been reported to contain chlorate (1 to 70 mg/L) (Warrington, 2002), but information about the potential for perchlorate release from these facilities is limited.

Other Sources

Some analytical laboratories in industry, academia, DoD, and the Department of Energy use perchlorate compounds or perchloric acid in their research work. Some detergents (Alconox[®], Alcotabs[®], Liquinox[®], and NeuTrad[®]) have been tested and shown to contain up to 2.5 mg/kg perchlorate (Trumpolt et al., 2005). Potassium perchlorate has been used in medical practice for the treatment of thyroid disorders. Sodium hypochlorite is used to disinfect water supplies, to treat pool water, and disinfect groundwater production wells. Household bleach also contains about 390 µg/L per bottle of perchlorate (Trumpolt et al., 2005).

2.3.2.3 Navy Sources of Perchlorate

Navy munitions containing perchlorate include solid propellant rockets and missiles, munitions, and explosives (black powder, nitric acid). Perchlorate is a known component of torpedo warheads, solid fuel rockets, underwater mines, aircraft countermeasure equipment, jet-assisted takeoff (JATO) devices, fixed ammo, pyrotechnics, training guide missile simulators, rocket motors, chaff IR decoys, signal flares, parachute flares, hand grenades, incendiary bombs, tracer rounds, smoke grenades, fuzes, thermite-type incendiaries, illumination signals/rounds, smoke signals, and ammunition (California Department of Toxic Substances Control, 2013). The number of items and amount of perchlorate in these materials is largely site-specific and subject to the availability of any historic records and/or potential results of environmental efforts.

2.3.3 Release and Alteration in the Environment

Perchlorate may be released into the environment in the form of different salts, including ammonium perchlorate, potassium perchlorate, sodium perchlorate, and others. All dissolve readily into water, though the maximum solubility of the various salts may vary slightly. Perchlorate may also be released into the environment as a liquid matrix, such as in solution with water, concentrated brine, or perchloric acid. This form of perchlorate increases the potential, as well as the speed of a spill reaching groundwater or surface water.

Perchlorate can potentially enter the air from natural sources, in addition to anthropogenic production, use, and accidental spills during loading and unloading for shipment, or during transport. Perchlorate compounds have negligible vapor pressures but can exist in air for a short time as particulate matter. Perchlorate-containing particles are removed from the atmosphere mainly by gravitational settling or by rain. Soil particulate matter containing perchlorate can be transported in air. The fate and transport of perchlorate in air is largely determined by the size and density of the particles and by wind speed and direction.

Environmental scientists have limited knowledge about the distribution of perchlorate in soil. What is known is that the perchlorate does not bind to soil particles appreciably and that the movement of perchlorate in soil is largely a function of the amount of water present. Perchlorate salts that are released to the soil in solid form will readily dissolve into whatever moisture is available. If sufficient infiltration occurs, the perchlorate will be completely leached from the soil. Plants can uptake perchlorate in soil moisture through the roots, and several ecological studies have demonstrated the tendency of some plants to concentrate the

perchlorate in plant tissues (Urbansky, 2000; Ellington et al., 2001). Some perchlorate may be held in solution in the vadose zone by capillary forces. In arid regions, crystallized perchlorate salts may accumulate at various horizons in the soil due to evaporation of infiltrating rainfall that leached perchlorate from shallower depths.

In dilute concentrations typically found in groundwater, perchlorate behaves conservatively, with the center of mass of the plume moving at the same average velocity as the water. Dispersion will cause the contaminant front to move faster than the average groundwater velocity. Perchlorate is kinetically very stable under environmental conditions and will not react or degrade in solution under ambient conditions. Biodegradation of perchlorate in groundwater will not occur unless significant levels of organic carbon are present, oxygen and nitrate are depleted, and perchlorate-degrading anaerobic bacteria are present. The combination of high solubility, low sorption, and lack of degradation tends to create plumes that are large and persistent.

Perchlorate release via highly concentrated brine solution in a groundwater system may be controlled by density effects (Flowers and Hunt, 2000). The density contrast between the brine and groundwater may cause the brine to move vertically with minimal influence by groundwater movement and little or no dilution. Brine pools may form on top of confining layers, and significant perchlorate mass may move into low permeability, confining layers by diffusion. The brine pools and perchlorate mass absorbed by the confining layers may create a long-term source of dissolved contaminant as perchlorate is released to the groundwater by diffusion. This type of release may occur where perchlorates have been manufactured at rocket motor washout facilities or other locations where perchlorate has been slurried or handled in concentrated brines.

The most common co-contaminants found at perchlorate-contaminated sites are nitrate and sulfate. Nitrate concentrations in contaminated media are generally far greater than those of perchlorate, and the presence of nitrate typically interferes with efficient reduction of the perchlorate anion. However, nitrate is commonly removed along with perchlorate because most perchlorate-reducing bacteria are denitrifiers as well (Logan, 2001). The presence of sulfate should not adversely impact perchlorate removal, as perchlorate is generally reduced before sulfate. However, if the redox potential is too low, sulfate may become the electron acceptor (ITRC, 2002). Additionally, co-contaminants such as sulfate, nitrate, bicarbonate, carbonate, and bromide can compete with perchlorate during ion exchange processes.

The presence of co-contaminants at perchlorate sites also can depend on facility-specific operations and historical practices. For example, many major weapons system with solid propulsion, explosive devices, or pyrotechnic devices contain perchlorate compounds. At such sites, typical co-contaminants also include volatile organic compounds (VOCs), halogenated VOCs such as trichloroethylene (TCE), solvents, and explosive compounds such as trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine (HMX) (ITRC, 2002). The presence of these compounds does make efficient perchlorate treatment systems more difficult to design.

2.4 PERCHLORATE ANALYSIS

2.4.1 Analytical Chemistry Methods

The two conventional EPA methods currently available for analysis for perchlorate in drinking water and other waters are Method 314.0 (U.S. EPA, 1999) and Method 9058 (U.S. EPA, 2000). Both methods are based on use of an ion chromatography instrument, but they differ in the preferred columns. Method 314.0 has more alternatives for cleanup (pretreatment) procedures to cope with interfering ions. Both methods include requirements for matrix spikes (also called "laboratory fortified sample matrices") to verify the performance of the method for the sample matrix involved. Such quality control (QC) samples are used to confirm that acceptable sample detection limits are attained. The main limitations of the methods stem from interference from other ions that can cause higher sample detection limits, false negatives, and false positives. To address these limitations, variations of these two current EPA analytical methods are under continuous development, which has resulted in the methods described below. A comparison of perchlorate laboratory methods is provided in Table 2-2.

U.S. EPA has several newer methods for the determination of perchlorate in environmental samples. Method 332.0, "Determination of Perchlorate in Drinking Water Using Ion Chromatography with Suppressed Conductivity and Mass Spectrometric Detection," came out in March 2005. This method substitutes an ESI-MS detector for the conductivity detector of Method 314.0. The inherent advantage of the new method is that the mass spectral data (especially the ratio of the concentrations of perchlorate ion masses of 99 and 101 daltons, which are derived from the two masses, 35 and 37 daltons, of natural chlorine) provide confirmation of the identity of the perchlorate or definite evidence of false positive results from interferents. This method can handle relatively high concentrations of total dissolved solids, but sulfate may still pose a problem. The natural abundance of sulfur-34 causes just over 4% of bisulfate ions to have a mass of 99 daltons, which distorts the perchlorate ion ratios. Some analytical methods use the 83- and 85-dalton masses, which correspond to the perchlorate ion, less one oxygen atom, to minimize interference.

Method 331.0, "Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry," was also released in 2005. This method, compared with Method 314.0, uses a different ionization and detection approach while still using a LC column to separate perchlorate from other ions, which may be more effective in reducing interference. The option for using tandem mass spectrometry (MS/MS) provides a tool to eliminate the sulfate interference problem. The method quantitates perchlorate against an isotopically labeled (oxygen-18) perchlorate internal standard. Although more expensive than standard ion chromatography with conductivity detection, Method 331.0 may provide the versatility needed for difficult matrices.

In addition, Method 314.1, released in May 2005, is a variation that uses a preconcentrator column to remove common interferents, including chloride, carbonate, and sulfate. It then provides for use of a second column to confirm the identity of perchlorate, as is done in Method 8081A and similar chromatography methods.

2.4.2 Rapid Screening Methods

Two commonly accepted field methods exist for evaluating perchlorate. One method uses an ion selective electrode and the other uses colorimetric techniques. Both of these approaches have benefits and limitations as described in Table 2-3.

2.4.3 Perchlorate Real-time Sensing for Site Mapping

Recently a real-time sensor was developed for evaluating perchlorate levels at a site using Surface Enhanced Raman Spectroscopy (SERS) (SSC San Diego, 2003; Mosier-Boss, 2011) and a Site Characterization and Analysis Penetrometer System (SCAPS) to map a site. While initially developed for sites with known perchlorate contamination at ppm (mg/L) levels, it is possible to extend the utility of this approach to evaluating a site for forensic purposes, such as when developing a site conceptual model and/or for targeting sampling locations for determining background perchlorate signatures. The sensor works by means of a perchlorate sensitive anion exchange resin film on a SERS substrate. More recently an extension of this technology has been the focus of development to provide a portable technology with enhanced SERS sensitivity for field analysis of perchlorate down to sub-ppb (µg/L) levels (SERDP-ESTCP, 2011).

2.4.4 Forensics Methods

In recent years, many studies have reported the presence of perchlorate in areas unanticipated to have a perchlorate signature at what appear to be background levels. This has facilitated investigations seeking to characterize and identify the origin of this apparently ubiquitous perchlorate signature, including both isotopic analyses and the evaluation of a range of associated environmental data and other analytes observed to be correlated with various synthetic or natural perchlorate sources (Table 2-4).

2.4.4.1 Environmental Quality Data and Analytes Potentially Associated with Perchlorate

The evaluation of general environmental quality data and other analytes (hereafter referred to as correlation analytes) is considered a starting point for potential source identification at a site. Such information can provide valuable clues as to the origin of a perchlorate signature, influencing what types of

advanced methodologies and strategies would best be employed for extended studies focused on specific or unique perchlorate sources. A selection of potential correlation analytes/groundwater (GW) data is shown in Table 2-4. In most cases, the analytes/data shown are unregulated and thus not necessarily quantified as part of an existing sampling and analysis compliance or monitoring program. A possible exception to this might be the evaluation of nitrogen (nitrate/nitrite) as a measure of nutrient loading, such as in a heavily used agricultural area or in an area of a watershed adjacent to such an area. It is important to note that a weight of evidence approach must be used in the context of the site characteristics, as not any one of the analytes or GW data illustrated may be sufficient to distinguish perchlorate sources.

Because the analysis of these correlation analytes is performed without prior knowledge about how the analytes may (or may not) be related to the perchlorate signature on the range, it is useful to employ a statistical treatment known as principal components analysis (PCA). PCA is a data simplification tool that is useful when one is attempting to evaluate a suite of variables (true variables) that appear to be unrelated in a dataset, but may actually contain a significant level of redundancy or similar behaviors. This approach allows one to identify those redundancies and combine them into single predictor or criterion variables known as principal components (artificial variables), comprised of similar true variable behaviors. This makes it much easier to ascertain which true variables in the original suite of variables are significantly independent of others, which in turn can assist with interpreting potential perchlorate sources. This will be illustrated during the case study in Section 4 with experimental correlation analyte data.

To associate observed perchlorate levels of 10 µg/L or less with a natural perchlorate source, one should analyze groundwater samples at a much lower perchlorate quantitation level. In addition, it is useful to measure groundwater samples for a suite of forensic analytes selected from Table 2-4 using conventional analysis with data evaluation suitable for potential correlations with perchlorate.

A 2009 study (Munster and Hanson, 2009a) assessed perchlorate and ion chemistry of road runoff, and showed correlation of certain ions with perchlorate. Auto exhaust contained B, Br, Ca, Mg, Na, N, K and Sr. Dust from brake pads contained Mg, Cl, and Ca. Bromide was present in fuel. Nitrogen was present in roadside fertilizers. Road flares contained mostly K, Sr, NO_3, and ClO_4; however, most of the NO_3 and ClO_4 would be consumed during use if they burn completely. De-icers contained mostly Cl, Na and Ca. The Cl to Br mass ratio of automobile exhaust with catalytic converters is 61, paved road dust and tire dust are both 30, and brake dust is 38. A fully burnt flare had a N-NO_3 to ClO_4 mass ratio of 24, while an unburned road flare had a mass ratio of 2. The N-NO_3 to ClO_4 mass ratio for Bull dog Soda, which is sodium nitrate derived solely from mined Chilean caliche, is 113 (Collette et al., 1999).

Perchlorate in urban lawn fertilizers also show similar relations to certain ions (Munster and Hanson, 2009b). This study showed that perchlorate is rarely detected in fertilizer products that do not contain caliche ore (Susarla et al., 1999; Urbansky and Collette, 2001). If the nitrite ion is in much higher concentration than the perchlorate ion, perchlorate degradation will not occur. Any increase in the perchlorate ion to Cl ratio from bulk precipitation indicates another source of the perchlorate ion besides precipitation because evaporation should not change this ratio.

Table 2-2. Comparison of perchlorate analytical laboratory methods (from ITRC, 2005).

Method (technique)	Applicability	Analytical limitations	Aqueous reporting limits (µg/L)
EPA 314.0 (ion chromatography [IC])	• Mandatory for drinking water samples reported under UCMR 1 • Aqueous samples with low dissolved solids (conductivity <1 mS/cm total dissolved solids [TDS]) and chloride, sulfate, and carbonate concentrations <100 mg/L each • Conductivity of samples must be below the laboratory's established matrix conductivity threshold	• Analysis is subject to false positives due the unspecific nature of the conductivity detector • Method has been validated in drinking water only; no guidance provided for use with soils, biota, etc. • The lower reporting limit of 0.5 ppb is achievable only in samples with very low TDS • Inappropriate for use in samples with high TDS	4
EPA 314.1 (IC)	• Method has been used on aqueous samples, including those with high TDS • Published EPA method (EPA 2005a) • Planned option for UCMR 2	• Analysis may be subject to occasional false positives due to the unspecific nature of the conductivity detector • Uses second dissimilar chromatographic column to aid in qualitative identification • Requires the use of anion reduction cartridges if used to analyze samples with high TDS	0.5–1
EPA 9058 (IC)	• Aqueous samples w/ <1 mS/cm TDS • Soil samples • EPA method published (EPA 2000a)	• Analysis may be subject to false positives due to lack of confirmation requirements or conformational chromatographic column • EPA method currently under revision	0.5–1
EPA 6850 (LC/MS)	• Aqueous samples to include those with high TDS • Soil samples • Biota samples • Determinative method for perchlorate • Published EPA method undergoing validation studies	• None reported	0.2 for water and soil; 0.6 for biota
EPA 331.0 (LC/MS or LC/MS/MS)	• Method limited to aqueous samples to include those with high TDS • Planned option for UCMR II • Determinative method for perchlorate • Published EPA method available (EPA 2005b) • Planned option for UCMR 2	• Pretreatment recommended in Winkler, Minteer, and Willey (2004) method • May be subject to false positives unless ion ratio monitored • Under MS/MS, method is highly selective, but may be subject to false negatives unless adequate separation from common anions is achieved	0.02
EPA 332.0 (IC/MS or IC/MS/MS)	• Method has been used on aqueous samples, including those with high TDS, and on milk and biota samples • Determinative method for perchlorate • Published EPA method (EPA 2005c) • Planned option for UCMR 2	• May be subject to false positives unless ion ratio monitored • Under MS/MS, method is highly selective but may be subject to false negatives unless adequate separation from common anions is achieved	0.1
FDA Method (IC/MS/MS)	• Fruits and vegetables, bottled water, and milk	• None noted in literature	0.5 (limit of quantitation)

Table 2-3. Comparison of perchlorate field methods (from ITRC, 2005).

Method (technique)	Applicability	Analytical limitations	Reporting limits
Ion-selective electrode	• Can potentially detect perchlorate in the low-ppb range • Potential for in situ sampling for groundwater monitoring wells • Commercially available models suitable for both field and laboratory applications	• Commercial availability of low-ppb electrodes unknown • Presence of ions can interfere with the perchlorate electrode	• Low ppb (as tested); 200 µg/L (commercially available) • Detection limit may be too high to be useful
Colorimetry	• Used for surface water, well water, bioreactor effluent, and soil extracts. • Method published: USACE ERDC/CRREL TR-04-8 (Thorne 2004)	• Humic and fulvic acids from soil surface or root zone may cause false positives, requiring cleanup • Presence of chlorophyll or machine oils causes false positives	• 1.0 µg/L

Table 2-4. Groundwater quality data, environmental data, and analytes potentially associated with various natural or anthropogenic (synthetic) perchlorate sources.

Correlation Analyte/Data	Type	Significance	Potential impact	References
Atmospheric Tracers (^{3}H, ^{3}He, ^{14}C, SF_6, CFCs)	GW age, recharge, infiltration timeline, land-use history	Natural (prior to mid-20th Century), synthetic (since mid-20th Century)	Agricultural, synthetic	Böhlke, 2009; Plummer, Böhlke, and Doughten, 2006
Nitrate	Co-analyte	Natural	Atmospheric, agricultural	Graham, 2008; Parker, Seyfferth, and Reese, 2008; Duncan, 2005
Nitrite	Co-analyte	Natural	Atmospheric, agricultural	Dasgupta, 2005
Sulfate	Co-analyte	Natural	Atmospheric, agricultural	Plummer, Böhlke, and Doughten, 2006; Parker, Seyfferth, and Reese, 2008; Dasgupta, 2005; Böhlke, 2009; Duncan, 2005
Chloride	Co-analyte	Natural	Atmospheric, evaporitic, agricultural	Plummer, Böhlke, and Doughten, 2006; Graham, 2008; Parker, Seyfferth, and Reese, 2008; Dasgupta, 2005; Böhlke, 2009; Duncan, 2005
Bromide	Co-analyte	Natural	Atmospheric	Plummer, Böhlke, and Doughten, 2006
Iodate	Co-analyte	Natural	Atmospheric	Plummer, Böhlke, and Doughten, 2006; Dasgupta, 2005
Iodide	Co-analyte	Natural	Atmospheric	Plummer, Böhlke, and Doughten, 2006
Specific Conductance	All ionic Co-analytes	General GW quality, Geochemical parameters	All sources	Plummer, Böhlke, and Doughten, 2006
Temperature	Water conditions	General GW quality, Geochemical parameters	All sources	Plummer, Böhlke, and Doughten, 2006
pH	Water conditions	General GW quality, Geochemical parameters	All sources	Plummer, Böhlke, and Doughten, 2006; Duncan, 2005

Table 2-4. Groundwater quality data, environmental data, and analytes potentially associated with various natural or anthropogenic (synthetic) perchlorate sources. (Continued)

Dissolved Oxygen and Other Gases (Ar, Ne, CH$_4$, N$_2$)	Water conditions, GW recharge-infiltration temperature	Natural, General GW quality, Denitrification, GW dating	All sources	Plummer, Böhlke, and Doughten, 2006; Dasgupta, 2005; Böhlke, 2009; Böhlke, 2002
Total Dissolved Solids	Water conditions	General GW quality	All sources	Plummer, Böhlke, and Doughten, 2006; Dasgupta, 2005; Duncan, 2005
Magnesium	Co-analyte	Natural, Synthetic	Agricultural, fireworks	Böhlke, 2009; Conklin, 1985
Strontium	Co-analyte	Synthetic	Fireworks	Böhlke, 2009; Conklin, 1985
Aluminum	Co-analyte	Synthetic	Fireworks	Böhlke, 2009; Conklin, 1985
Antimony	Co-analyte	Synthetic	Fireworks	Böhlke, 2009; Conklin, 1985
Barium	Co-analyte	Synthetic	Fireworks	Conklin, 1985; Böhlke, 2009
Sodium	Co-analyte	Synthetic	Fireworks	Conklin, 1985; Böhlke, 2009; Duncan, 2005
Potassium	Co-analyte	Synthetic	Fireworks	Conklin, 1985; Böhlke, 2009
Iron	Co-analyte	General GW quality	All sources	Conklin, 1985; Böhlke, 2009; Duncan, 2005
Calcium	Co-analyte	General GW quality, Synthetic	All sources, fireworks	Conklin, 1985; Böhlke, 2009; Duncan, 2005

When perchlorate is detected at low concentrations (< 10 µg/L) in groundwater, natural sources should be considered. Isotopic methods are powerful tools when applied to the intractable problems of source attribution for the most common groundwater contaminants, including nitrate, VOCs, and perchlorate. Radioactive isotopes can be used to determine groundwater age, or the time since water entered the saturated zone, which has important implications for delineating groundwater or contaminant flow pathways, identifying recharge areas, and providing a measure of aquifer vulnerability. The age of groundwater (time since filtration or recharge) is an important forensic tool for ClO_4^- that may be either natural or anthropogenic in origin, particularly given that much of the known synthetic ClO_4^- contamination in the U.S. occurred after the 1940s.

Groundwater age approaches have been summarized as follows (Hatzinger, Böhlke, Sturchio, and Gu, 2011). Measurable groundwater ages in aquifers commonly range from years to millennia and therefore can be used to relate ClO_4^- occurrences to land-use history. Groundwater ages can be determined up to 60 years by analyzing atmospheric environmental tracers, including tritium, sulfur hexafluoride, and chlorofluoro-carbons, all of which, like perchlorate, have been incorporated in groundwater in varying concentrations since the mid-1900s. Analyses of helium-3 (^{3}He), from the decay of tritium (^{3}H), can also provide groundwater age estimates. Analysis of dissolved neon (Ne) is also conducted during tritium-helium age dating to evaluate degassing or the presence of excess air in samples. Groundwater ages on the order of 10^3 to 10^4 year can be estimated from concentration of ^{14}C, as was done in the southwestern United States to document the occurrence of natural (pre-anthropogenic) ClO_4- (Plummer, Böhlke, and Doughten, 2006;

Jackson et al., 2010). Descriptions of collection and interpretation of groundwater-age data are described in several publications (Cook and Herczeg, 2000; Busenberg and Plummer, 1992, 2000), with additional details in the following sources and references therein (Thatcher, Janzer, and Edwards, 1976; USGS, 2011).

2.4.4.2 Perchlorate Isotopic Analysis

Research is also being conducted to develop methods for directly differentiating between naturally occurring and man-made perchlorate in the environment. One approach is to use stable isotope ratio analysis of the perchlorate molecule. Stable isotope ratio analysis relies on the fact that the major elements composing the inorganic molecules occur as isotopes that can be quantified using IR-MS. The ratio of the specific isotopes in the perchlorate molecule, chlorine and oxygen, can be used to track the source of the perchlorate in the environment (Bao and Gu, 2004). Details and reviews of stable isotope terminology and general principles can be found in the literature (Hunkeler et al., 2008; Sharp, 2007; Clark and Fritz, 1997; Kendall and Caldwell, 1998; Coplen, 1994), but a summary is provided as follows.

Isotopes of a given element have the same number of protons and electrons, but a different number of neutrons that provide mass but no charge, defining the different isotopes. Methods for stable isotopic analyses of ClO_4^- are related to the stable isotopes of Cl and O, unlike the unstable isotopes that are subject to nuclear decay (radioactive). Isotopes can exhibit slightly different physical, chemical, and biological behaviors, which undergo differential processes in the environment that can alter their relative abundances in a given chemical compound. This process is called "isotopic fractionation," which can be mass dependent or non-mass-dependent resulting in different samples with distinct isotopic compositions indicative of the origin of a molecule. This itself has forensic science applications (Beneteau, Aravena, and Frape, 1999) and additionally provide a means of tracking systematic changes to a molecule during degradation processes in the environment. Detailed explanations of isotopic analysis processes and how they work are summarized in Hatzinger et al. (2011) and Leeson et al. (2007).

Data collected reveal that the chlorine isotope ratio in a naturally occurring perchlorate source is considerably lower than that in synthetic perchlorate. Conversely, the oxygen isotope ratio for the natural perchlorate is appreciably higher than in man-made sources. Researchers at Louisiana State University and Oak Ridge National Laboratory (ORNL) were on the early developmental forefront in this technique (Erickson, 2004). Some locations may have a mixture of man-made and naturally occurring perchlorate. The western half of the United States would appear to represent the most likely area for mixed plumes to occur due to favorable geological and precipitation conditions.

Recently, research conducted under the DoD Environmental Security Technology Certification program has demonstrated that chlorine isotope ratio ($^{37}C/^{35}Cl$, reported as $\delta\ 37\ Cl$) in the naturally occurring perchlorate derived from Chile is considerably lower than that of man-made perchlorate, irrespective of manufacturer, and the oxygen isotope ($^{18}O/^{16}O$, reported as $\delta^{18}O$) ratio for the caliche-derived material is appreciably higher than for the synthetic materials. This was true for both the caliche mineral and for fertilizers produced and imported from this mineral. The observed ^{17}O excess, which is presumably derived from the formation of perchlorate from ^{17}O-enriched ozone in the upper atmosphere, has not been detected in any synthetic samples of perchlorate. Thus, ratios of three stable isotope ratios ($^{37}Cl/^{35}Cl$, $^{18}O/^{16}O$; $^{17}O/^{16}O$) differ significantly between natural Chilean perchlorate and man-made perchlorate (Böhlke et al., 2005).

Stable isotope ratio analysis mostly depends on the matrix and concentration of perchlorate present. Solid samples typically require multi-step cleanup procedures to eliminate the presence of other non-perchlorate oxygen sources. Also, the concentration of perchlorate in trace-level aqueous samples may be too low initially for isotopic analysis and require concentration on an ion exchange resin. The distinction that can be identified through stable isotope ratio analysis is between perchlorate that forms by natural environmental processes and perchlorate that is manufactured through an industrial electrolytic process. Anthropogenic perchlorate that was released to the environment by using products manufactured from material containing naturally occurring perchlorate (such as Chilean nitrate) will likely have the same stable isotope ratio as other natural environmental occurrences of perchlorate.

Isotopic analyses can be performed at several U.S. government and academic laboratories with R&D analytical capabilities, but few contract laboratories offer this type of analysis (RITS, 2005):

- USGS Reston Chlorofluorocarbon Laboratory
- Universities:
  University of Chicago
  University of Arizona
  University of Nevada
  University of Maryland
- National Laboratories
- Some commercial vendors

The continued evolution of analytical forensic techniques may permit the fingerprinting of detected perchlorate plumes to ascertain whether the source is natural or manmade and to what extent each source type is represented. As technologies for perchlorate forensics become more mature, the SCAPS technology for site mapping described in Section 3.4.3 may be a realistic platform for such analyses.

2.4.5 Other Laboratory Techniques

Capillary electrophoresis (CE) has been used to analyze perchlorate for certain applications (primarily forensics). CE is not currently viable for analysis of perchlorate in environmental media at low concentrations. The best limit of detection available with most widely available equipment and reagents for CE is approximately 100 µg/L (Urbansky, 2000).

3. SITE STUDY DESIGN FOR PERCHLORATE FORENSICS

The broad approach to evaluating a site for perchlorate forensics analysis is illustrated in Figure 3-1. The three initial primary components that should be developed or evaluated at a site are (1) the presence of perchlorate (analytical data), (2) the historical use of perchlorate (contaminant site use summary, CSUS), and (3) the conceptual site model (CSM). These components may already exist as part of ongoing site efforts or may require data mining or perhaps even some additional perchlorate sampling and analysis of environmental media from the site for screening purposes. It is important to quantify and document, or at least provide some degree of confidence in the information or data used to assess each of these three components for the site.

Once the decision is made to proceed with a forensic investigation using the above approach, a site assessment can then commence in the context of the generalized contaminant source identification (CSI) framework that was provided in Figure ES-1 and ES-2. The CSI framework broadly provides the user with the types of forensics questions that should be addressed and how the forensics analysis should be applied within the context of the CSM and CSUS at a given site for a given contaminant.
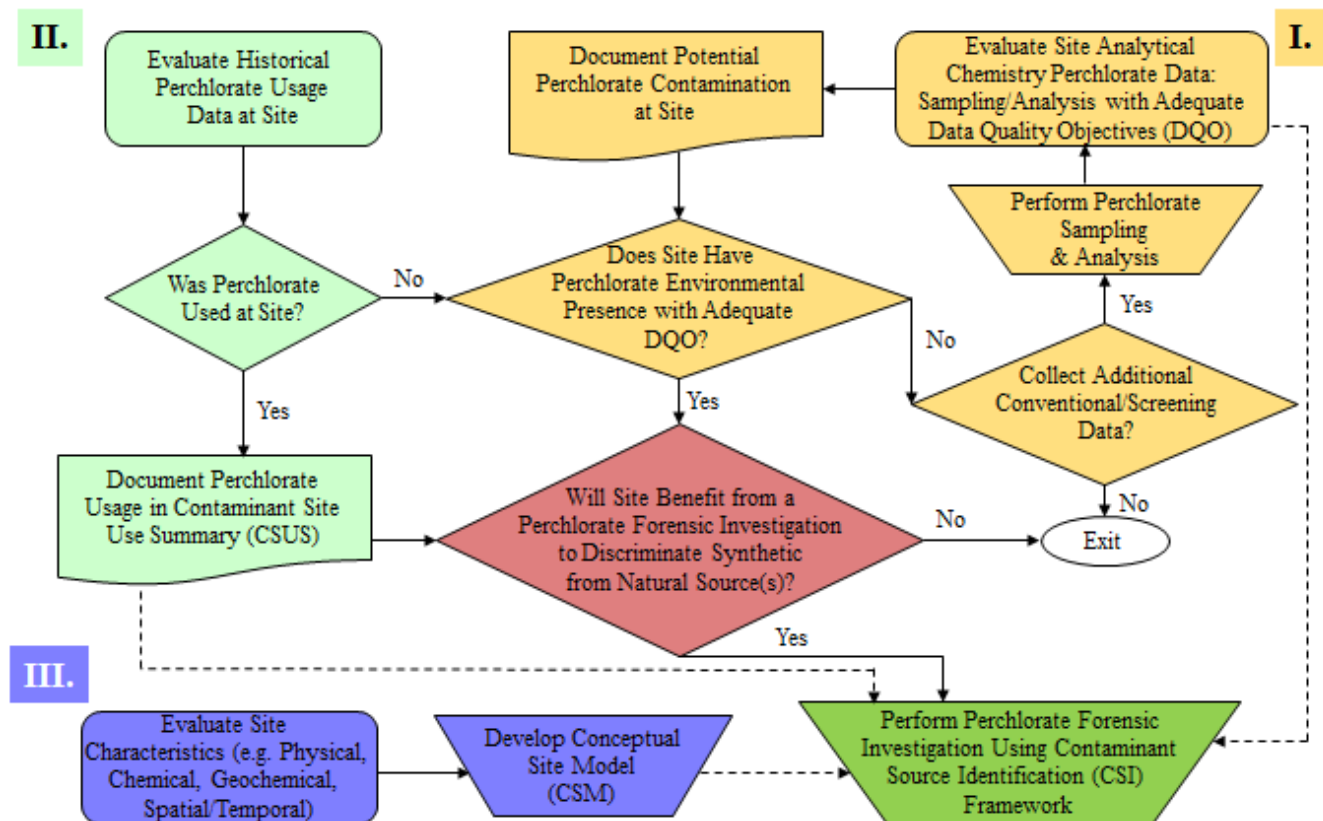
Figure 3-1. Perchlorate site forensics flowchart. Components I and II determine if the site might benefit from a perchlorate forensics investigation. Once this determination is made, data and information from all three components (I, II, and III) are incorporated into the perchlorate forensics investigation, i.e., using evaluations of site perchlorate analytical data, historical usage data (CSUS), and conceptual site model (CSM), as described in the text.

To best illustrate the use of the above flowchart, CSI framework, and assessment, a site was selected as a case study, and undertaken as part of this technical guidance development effort. For feasibility (cost and timeline) considerations, the starting point would be to use a range site that was already undergoing some level of perchlorate evaluation and monitoring as part of the Navy's range condition assessment (RCA) efforts.

3.1 EVALUATING A SITE'S POTENTIAL FOR FORENSIC STUDY

The following sites were considered for background perchlorate evaluation, as all would benefit from such an effort (as confirmed with responsible end-users/managers at the sites): NAF-El Centro (California), Pinecastle Range (Florida), and Boardman Range (Oregon). These sites were initially evaluated in this effort as a potential case study for background perchlorate source evaluation. The Pinecastle Range shown in Figure 3-2 appeared to be best suited for this evaluation. The case study results for this site are presented in Section 4.

It is anticipated that end-users will identify the sites described (Boardman Range, NAF El Centro, or other ranges and facilities) for evaluation in the later phases of the effort to fully demonstrate/validate the developed approach/methodology. Further site evaluations would be coordinated with ongoing site assessments and requirements as they are developed.

If interested only in the Pinecastle Range and case study results, after reading the background on Pinecastle in Section 3.1.1, the reader can skip ahead to Section 4.

3.1.1 Pinecastle Range

This site is part of ongoing efforts under the range sustainability environmental program assessment (RSEPA) process. The following synopsis and map is excerpted from the Jacksonville Range Complex Management Plan (U.S. Fleet Forces Command and NAVFAC Charleston, 2007).

The Pinecastle Impact Range is located in north central Florida. The range lies approximately 80 nmi (92 mi) south of Jacksonville, Florida, and 32 nmi (37 mi) inland of Daytona Beach, Florida. The range is located on Ocala National Forest lands and operates under a special use permit issued by the United States Department of Agriculture (USDA) Forest Service. The range accommodates air-to-ground (A-G) delivery of inert and live ordnance, strafing, and laser training. It is the Navy's only east coast A-G impact area cleared for live ordnance use. The range offers various target types, including those that simulate targets that would be encountered in a real military action. An aerial photograph of the Pinecastle Range and its targets is shown in Figure 3.3. Land surrounding the range property is forested in pine. Target areas are cleared, as are access corridors connecting the individual targets. The Pinecastle Impact Range, shown in Figure 4-1, has seven impact areas that will be discussed in Section 4. The Pinecastle Impact Range lies within R-2910 (discussed below). The range and R-2910 are encompassed by the Palatka 1 military operating area (MOA). The Navy Primary Mission Area supported by the Pinecastle Impact Range and associated special use airspace (SUA) is Strike Warfare (STW). R-2910, which designates surface and layered airspace within the Palatka 1 MOA that encompasses the Pinecastle Impact Range targets. R-2910 is further divided into three areas (R-2910A/B/C) with varying altitude restrictions.

The War Department (WD) acquired 40,587 acres for the former Lake Bryant Bombing and Gunnery Range in the early 1940s. On 27 June 1941, the WD acquired use of 23,167 acres for an Army bombing and gunnery range by means of a temporary use permit from the USDA. By two Memoranda of Understanding with USDA, the Army acquired more land in the same area: 3,354 acres by transfer and another 14,066 acres by conveyance bringing the total to 40,587 by 11 January 1943. The United States Armed Forces Command used the Lake Bryant Bombing and Gunnery Range during World War II. The range was under the jurisdiction of Pinecastle Army Air Field (AAF) and the Orlando Army Air Base. The site was also known as the Ocala Bombing Range, the Ocala Bombing and Gunnery Range, the Ocala Aerial Bombing and Gunnery Range, and the Ocala Range. The site was used for practice bombing, including the use of high explosive general purpose (HE/GP) bombs, AAF Board Projects, ground gunnery and rocket missions. There were also training facilities for firefighting details. Observation towers were constructed on the site along with a camp area for the fire fighters. At the conclusion of World War II, the WD determined the site was no longer required. It was declared surplus on 2 December 1956. The entire 40,587-acre site was relinquished back to the USDA by letter of transfer dated 20 May 1947. Of these 40,587 acres, 5,765 acres are not eligible for the Army Corps of Engineers' Defense Environmental. Restoration Program. (DERP) Formerly Used Defense

Sites. (FUDS) program because the Navy currently uses these acres for an active training site, the Pinecastle Impact Range.

A low-level perchlorate signature has been observed in groundwater, which is suspected to originate from a non-Navy source. These data will be described in Section 4 within the context of the perchlorate site forensics flowchart (Figure 3-1).
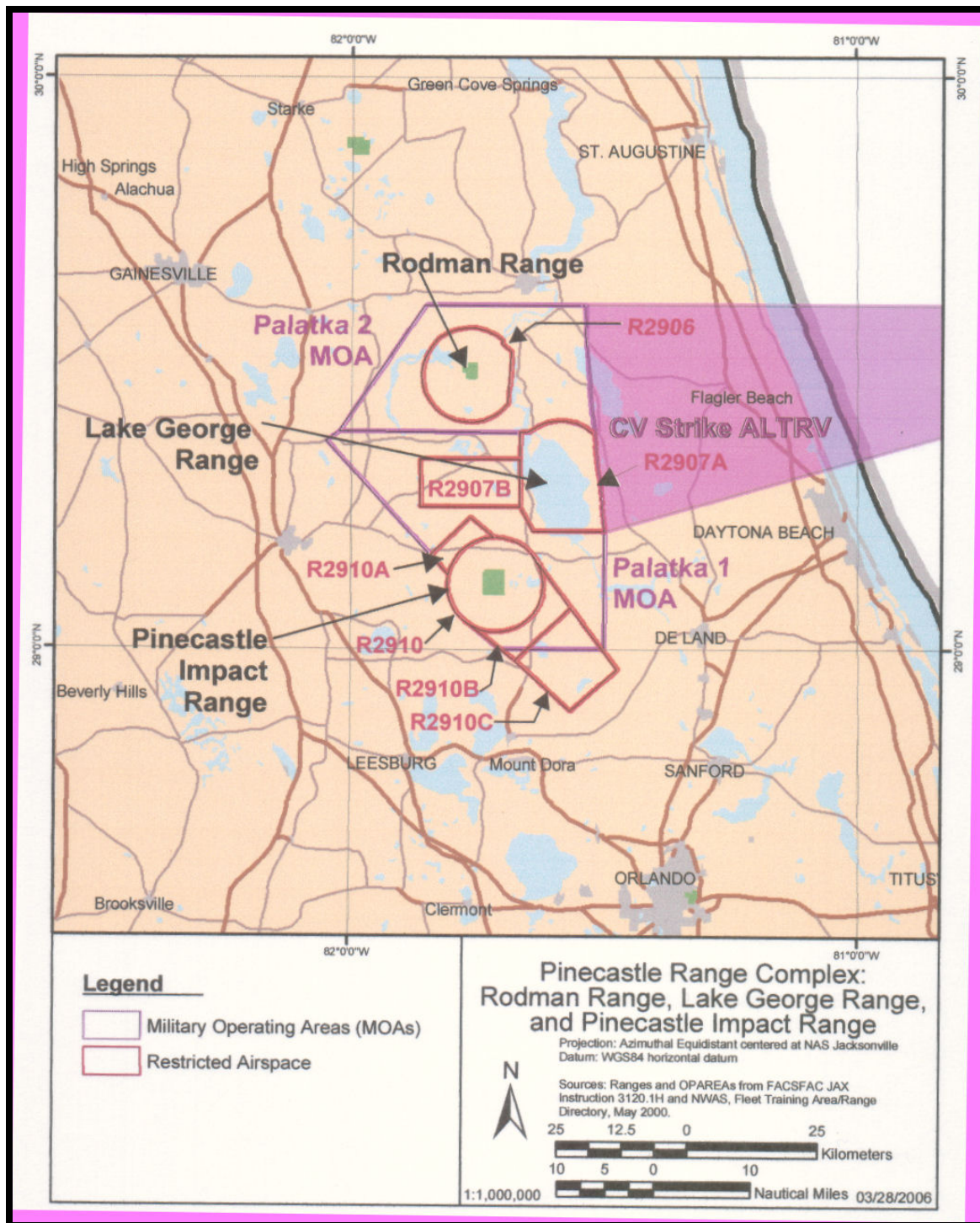

Figure 3-2. Pinecastle Impact Range in relation to other nearby ranges (Rodman Range and Lake George Range). Source: U.S. Fleet Forces Command and NAVFAC Charleston, 2007.
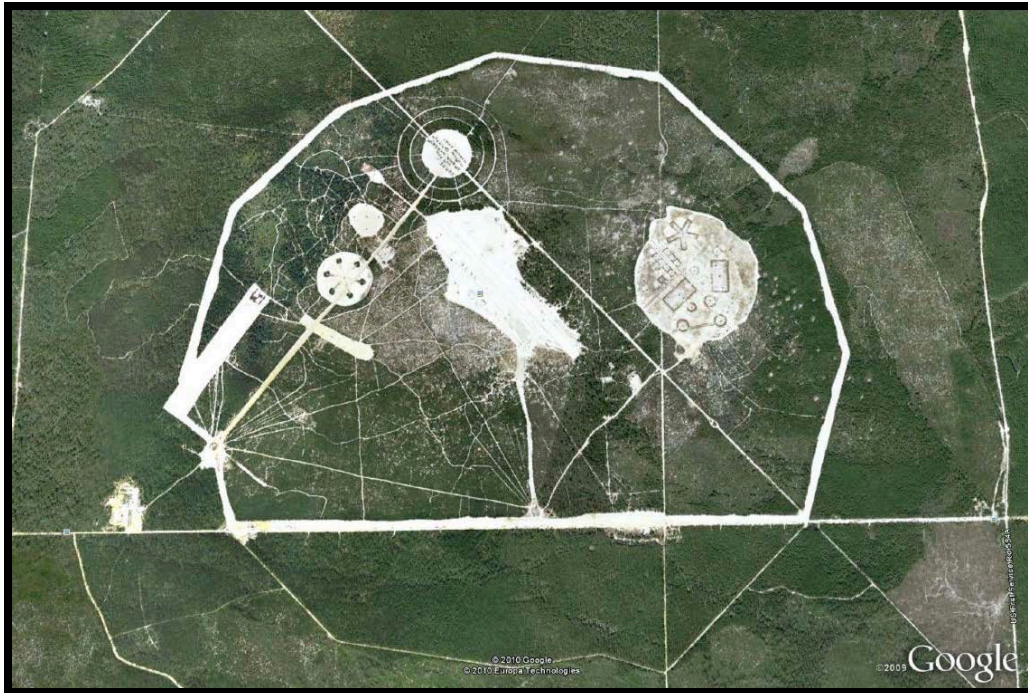
Figure 3-3. Aerial view of Pinecastle Range. Map data: ©2010 Google. ©2010 Europa Technologies.

3.1.2 Boardman Range

In addition to ongoing assessment efforts under the RSEPA process, this site was originally considered for a preliminary perchlorate effort (supported by Fleet Forces Command), focused on data mining/archival records and development of a conceptual site model (CSM). The expected follow-on effort was to be focused on evaluating the presence and levels of perchlorate in soils, but because the area was already the subject of numerous ongoing studies, a decision was made to use the limited funds for evaluating perchlorate on Pinecastle Range instead. The following synopsis and image is excerpted from the Northwest Training Range Complex Management Plan (U.S. Fleet Forces Command, U.S. Pacific Fleet, and NAVFAC EFA NW, 2007).

Naval Weapons Systems Training Facility (NWSTF) Boardman is located in north central Oregon near the Columbia River. Boardman consists of 47,982 acres of relatively flat, mostly bare, landscape. The land area is predominantly rectangular, 12 by 6 mi as depicted by the shaded blue rectangle in the inset of the aerial view of the range (Figure 3-4). Several A-G targets remain in the range, although their scoring systems have been removed. R-5701 and R-5706 and Boardman military operating areas (MOA) are located on top of NWSTF Boardman. The Oregon National Guard (ORNG) frequently uses Boardman for small arms live fire training by infantry and helicopter door gunners. NWSTF Boardman is an inshore area consisting of the following areas

- Boardman Military Operating Area
- Restricted Area 5701 (R-5701) (A/B/C/D/E)
- R-5706
- Bombing Range

A directive was issued in 1941 to acquire lands for the precision bombing range Boardman Air Force Range, initially known as Arlington Bombing Range. From 1941 to 1943, the War Department acquired 58,662.90 acres of fee; 37,320.31 acres of public domain lands (PDLs); and an easement for 2.30 acres. This totals 95,985.51 acres. From 1941 to 1945, the U.S. Army Air Corps used the range for precision bombing.

Walla Walla Army Air Base used the site for A-G gunnery practice. After World War II, the U.S. Army categorized the site as surplus land.

Figure 3-4. Boardman Range area. U.S. Fleet Forces Command et al., 2007.

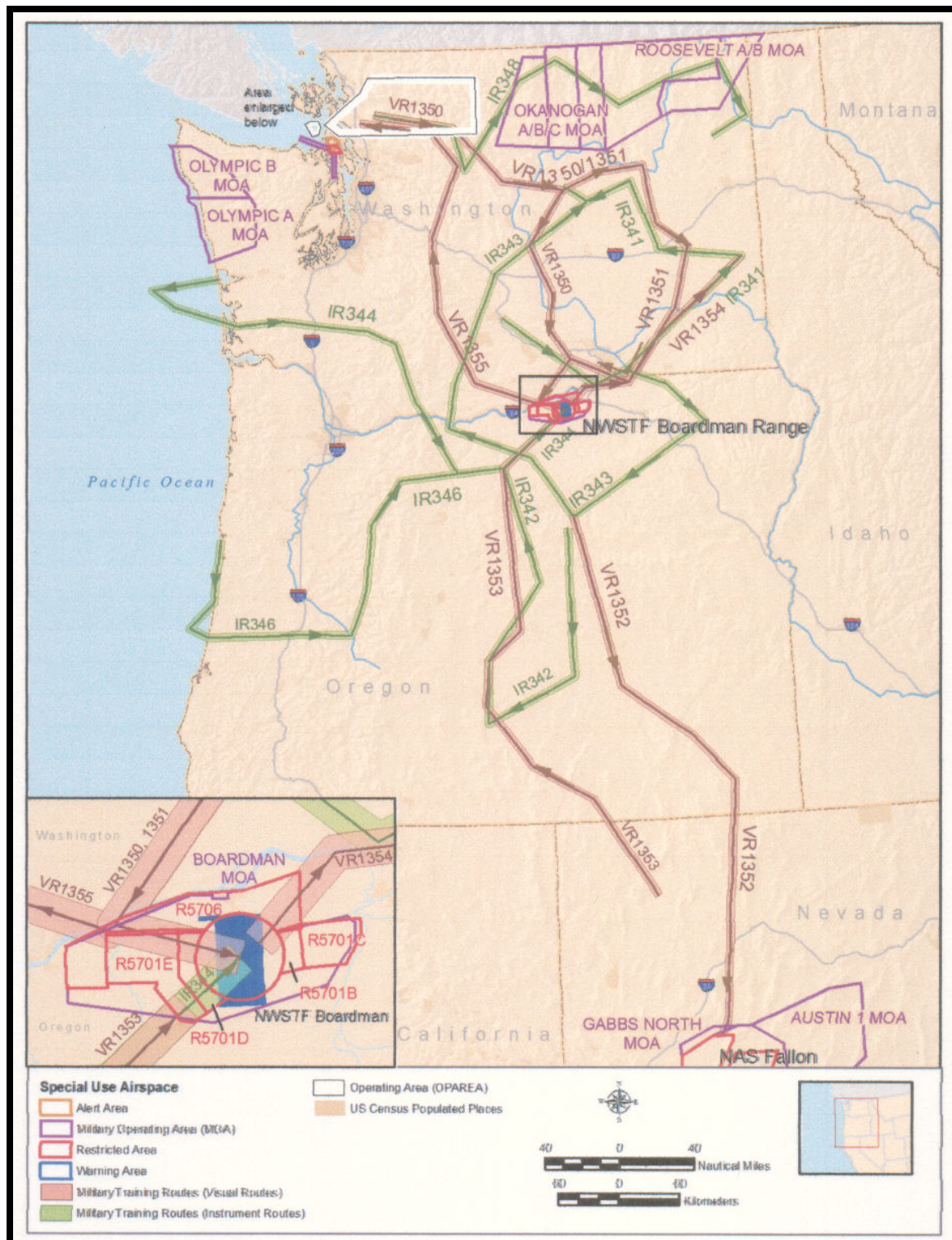In 1948, the Air Force withdrew the lands from surplus and continued using the site as a precision bombing range until 1960. Between 1952 and 1956, the 57th Air Division, Fairchild Air Force Base, assumed the responsibility, control, and utilization of the Boardman Range. The Department of Defense

(DoD) improvements to the site consisted of approximately 20 buildings, a flight strip, gunnery range, and numerous target sites. The Air Force declared the entire site as excess on 11 August 1960. On 22 November 1960, the Air Force transferred 58,372.90 acres fee and 2.30 acres easement to the Department of the Navy, 37,320.31 acres to the Department of Interior, and 290 acres to the U.S. Army Corps of Engineers (COE). The initial transfer divided the range into a checkerboard pattern that was not conducive for use as a modern bombing range. After several years of negotiating with the State of Oregon, a decision was reached to split the former range into two halves. The Navy consolidated its operation on the eastern 47,722.07 acre half, which they are currently using as a high-speed aerial bombing range; the Navy currently uses 37,320.31 acres of PDLs. The western half of the site eventually became jointly owned by the State of Oregon, Portland General Electric, and Morrow County. The 290 acres controlled by the COE was eventually decreased to 13.88 acres with the remaining 276.12 acres transferred to the State of Oregon.

3.1.3 Naval Air Facility (NAF)-El Centro

This site is the subject of ongoing litigation concerned with potential perchlorate migration from a range target area onto an adjacent commercial property. The following synopsis (Global Security, 2008) and Figure 3-5 (Battelle, 2007) have been included to describe the range complex.
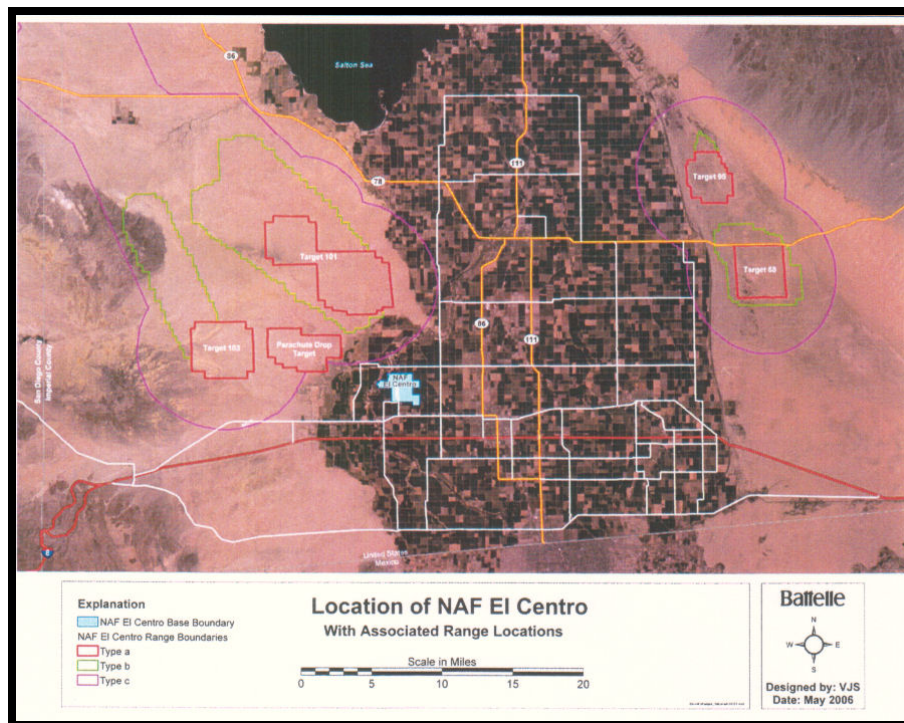
Figure 3-5. Ranges at NAF-El Centro. Source: Batelle, 2007.

Naval Air Facility-El Centro (NAF-El Centro) was commissioned on 1 May 1946 as a naval air station. Prior to that, the base was a Marine Corps Air Station. Through the years, NAF-El Centro has had several names: Naval Air Facility, Naval Auxiliary Landing Field, Naval Air Station, and the National Parachute Test Range. The NAF-El Centro Complex is located in Southern California's Imperial Valley near the Salton Sea, approximately 65 nmi east of San Diego, California.

The complex is considered part of the Southern California (SOCAL) (Inland) complex. The NAF-El Centro Complex is composed of the following target and instrumented areas:

- Target 101 "Shade Tree" (R-2510)
- Target 103 "Loom Lobby" (R-2510)
- Target 68 "Inkey Barley" (R-2512)

The following targets are associated with the NAF-El Centro complex; Military Operating Area (MOA), Air Traffic Control Airspace (ATCAA), and parachute drop zones:

- Target 95 "Kitty Baggage" (R-2512)
- Kane East–West-South MOA/ATCAA
- Bullhead, Camelot, Superstition Drop Zones (R-2510)

NAF-El Centro provides realistic training to active and reserve aviation units and activities of the Navy's operating and training forces. Squadrons visit NAF-El Centro to practice gunnery, bombing, carrier landings and air combat. The facility has two operating runways. The 9,500-foot east/west runway handles 96 percent of the traffic. It is equipped with a Fresnel Lens Optical Landing System at each approach end as well as lighted carrier deck landing areas at both ends so pilots can simulate carrier landings. NAF-El Centro is the "winter home" of the world-famous Blue Angels, the Navy's Flight Demonstration Squadron. Starting every January, the "Blues" conduct over two months of intense flight operations prior to the start of their air show season.

3.1.4 Other Potential Sites

In California, other potential sites of interest at the time of case study site selection include the following (Trizinsky, 2008):

3.1.4.1 Former MCAS El Toro

This former installation has one confirmed perchlorate release from IR Site 1 – Explosive Ordnance (EOD) training range, but the general area also appears to have widespread perchlorate background (possibly due to widespread historic use of Chilean nitrate fertilizers in the former agricultural areas in this portion of Orange County. Background studies might be helpful here when establishing cleanup targets. The final Remedial Investigation Report was released in December 2006. The major concern to date includes a groundwater plume of perchlorate discovered beneath the range and migrating down gradient onto Site 2. A draft Feasibility Study (FS) was submitted in January 2007. The FS for soils and munitions and explosives of concern will be finalized and a decision on remedial actions for these media is planned. Pilot studies field work on potential in-situ remedial technologies for groundwater are in progress. A FS that addresses groundwater contamination at Sites 1 and 2 will be finalized following the pilot studies.

3.1.4.2 Morris Dam

This former leased property, located in northern Los Angeles County, has perchlorate detections in soil and groundwater. The site is surrounded by a drinking water reservoir that has low levels of perchlorate in surface water. However, there appears to be a potential for a natural source in the area, as upstream surface water samples in the National Forest have yielded perchlorate concentrations ~ 3 times that of the surface water samples collected in the reservoir ~ 2 mi downstream. There does not appear to be a potential anthropogenic source in this upstream area. The project team has delineated a soil hotspot for perchlorate and other COCs was physically removed in 2010, but it seems unlikely that the Navy's hotspot is the source of the perchlorate detections in the drinking water reservoir (San Gabriel Tribune, 2010).

3.1.4.3 Naval Air Weapons Station China Lake

NAWS China Lake is an active installation in the Mojave Desert (San Bernardino, Inyo, and Kern Counties), adjacent to Ridgecrest, California. It does have some perchlorate releases impacting shallow groundwater, but the groundwater is unsuitable for beneficial use. NAWS China Lake also appears to have widespread naturally occurring perchlorate. Numerous evaporite deposits are in the area, and perchlorate has been detected at significant concentrations where no perchlorate activity has occurred. Background studies would be useful to establish reasonable clean targets for soil.

4. SELECTED CASE STUDY – PINECASTLE RANGE

4.1 SITE ASSESSMENT - EVALUATION USING THE CONTAMINANT SOURCE IDENTIFICATION FRAMEWORK

4.1.1 Background or Conceptual Site Model (CSM)

The Pinecastle Range Complex (see Figure 4-1) is located within the Ocala National Forest of central Florida, and on property owned by the United States Department of Agriculture (USDA) and managed by the United States Forest Service (USFS). It was originally part of the Lake Bryant Bombing and Gunnery Range. The Lake Bryant Range was operated by the U.S. Army between 1941 and 1947, before being acquired for use by the Navy as Pinecastle Range in 1951. The Navy has continuously operated the range under a special use permit since that time.

4.1.2 Geological Condition

The range lies in a geographical area of nearly flat terrain. No surface water bodies, wetlands, or springs are present within the target and buffer of the range; however, several lakes lie within 3 mi east of the target and buffer, Farles Lake (1 mi), Buck Lake (2.25 mi), Chain O'Lakes (2.25 mi), and Sellers Lake (2.75 mi). The closest springs to the target and buffer are Alexander Springs (~ 7 mi southeast) and Juniper Springs (~ 3 mi north). The nearest wetland is Farles Prairie, associated with Farles Lake, 1 mi east (U.S. Fleet Forces Command, 2002).

Surface soil, based on a 1998 groundwater assessment[2] and EnSafe field activities, as described in this report, consists of quartz sand, with occasional lenses of clay, silty clay, or clayey sand. Due to the high sand content, precipitation infiltrates rapidly after a rain event. The sandy soil supports sparse vegetation consisting of sand grass, pine, and dense shrubs, which are adapted to a high level of disturbance. Designated areas such as targets, roads, and fire lanes are maintained clear of vegetation as part of the range's maintenance and safety program. Of the 5,698 acres, the cleared target areas total 383 acres.

The uppermost sand geological unit generally ranges from 26 to 75 ft in thickness before a vertical facies change is noted, with sediments fining downward into a clayey sand and/or sandy clay. During historical studies, the clay layer was not observed in borings performed at the southwest corner of the range, suggesting that the unit is laterally discontinuous.

4.1.3 Hydrological Condition

Three major hydrogeologic units are in the study area, the Surficial Aquifer System comprising undifferentiated deposits, the intermediate confining unit consisting of the Hawthorn Formation, and the Floridan Aquifer System. Please refer to Figure 4-2 throughout the descriptions that follow (reproduced from the Comprehensive Range Evaluation report (NAVFACSE and EnSafe, 2009).

The surficial aquifer is differentiated from the underlying Floridian system, primarily on the basis of its composition of unconsolidated siliclastic sediments of Pliocene to recent age (Adamski and Knowles, 2001; Miller, 1986). The aquifer is also predominantly unconfined across the region, except in areas where lower permeability deposits (i.e., peats and organic clays) are found at ground surface and serve to locally semi-confine the underlying sediments. The surficial aquifer is recharged via direct infiltration of precipitation. Groundwater in the aquifer flows laterally to discharge into streams and lakes, when present. However, because the clean quartz sand deposits that comprise much of the surficial aquifer are exceptionally well drained, groundwater flow can have a significant vertical component.

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[2] Water & Air Research, Inc. 1998. "Groundwater Assessment Report for Pinecastle Bombing Range." Memorandums dated October 13, 1998 and July 31, 1998. Ocala National Forest, Florida.
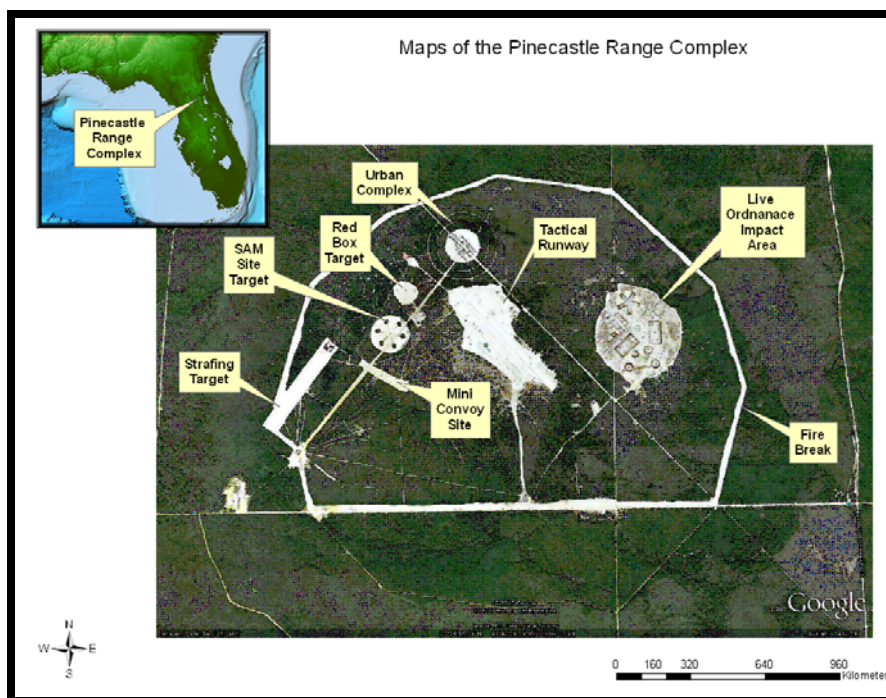
Figure 4-1. Maps and aerial view of the Pinecastle Range Complex. Source: Naval Facilities Engineering Command Southeast and EnSafe Inc., 2009.
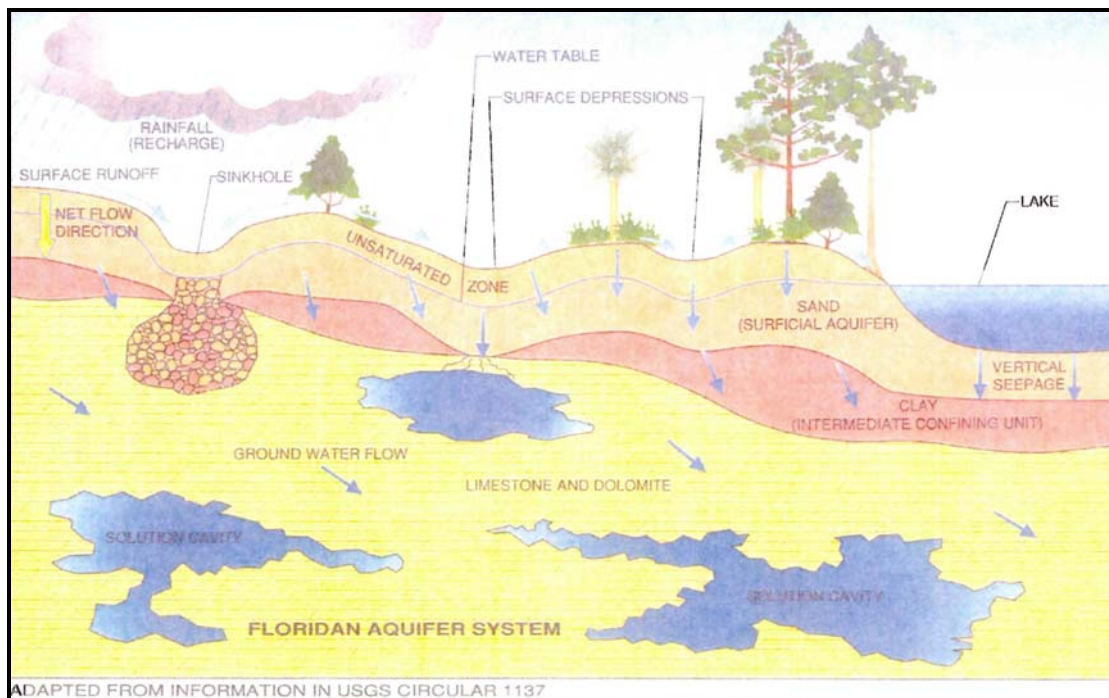
Figure 4-2. Hydrogeological characteristics of Pinecastle Range. Source: NAVFAC and EnSafe, 2009.

The surficial aquifer is separated from the underlying Floridan Aquifer System by the intermediate, confining Hawthorn unit, which contains clastic and low-permeability carbonates (limestones and dolomites). The unit's thickness in the Marion and Lake County area varies between 20 and 100 feet (Adamski and Knowles, 2001). Where sand and carbonate units are present, the intermediate aquifer may have enough permeability to support water (Adamski and Knowles, 2001; Scott, 1992). The intermediate confining unit's ability to retard vertical groundwater flow is highly variable. When fine-grained and clayey sediments are the predominant lithology, the unit can behave as a somewhat effective confining unit.

The Floridan Aquifer System, which underlies the intermediate system, exhibits two active permeable zones, the Upper and Lower Floridan Aquifers. These two active zones are typically separated by a middle confining to a semi-confining unit, depending upon locale. When no middle confining unit is present, the aquifer system is referred to as the Upper Floridan Aquifer (UFA) (Miller, 1986). Depth to the Floridan aquifer ranges between less than 100 to 200 ft and thickness ranges between 50 to 200 ft, throughout the Ocala National Forest and Lake County. Recharge to the Floridan Aquifer System is derived primarily from leakage from overlying units. Recharge rates may exceed 12 in per year in much of the Ocala National Forest (Osburn, Toth, and Boniol, 2002; SJRWMD, 2002). The Floridan aquifer discharges in areas generally east of the Ocala National Forest and follows the south–southeast trend of the St. Johns River, while other discharge areas coincide with lakes.

Because of the availability of high-quality groundwater from the Floridan, surficial groundwater is not typically used as a primary water source in the region. It does, however, discharge to lakes in the area, and is therefore potentially used for recreational purposes (boating, fishing, and swimming). Due to the extensive size of the Floridan Aquifer System (approximately 100,000 square miles) and its abundance of fresh water, it is the principal source of potable water supply for several southeastern states, including Florida, Georgia, South Carolina, and Alabama. Approximately 90% of Florida's population uses the Floridan Aquifer System for drinking water.

4.1.4 Operational Use

The Navy is authorized to operate and utilize the range under a special use permit for an additional 20-year period that began 1 August 2002. As a condition of the permit and to support the USFS land-use management plan in the range area, the Navy agreed to prepare and implement a groundwater monitoring

program to assess whether munitions constituents (MC) have impacted shallow groundwater migrating off the range.

The range consists of two separate areas for airborne training activities (Figure 4-1): (1) the Centroid, and (2) the impact area and associated buffer. The Centroid area, approximately 3 mi northeast of the impact and buffer boundary, houses the range control center. The target area comprises a relatively small amount of the range property, with combined impact and buffer areas that span 5,698 acres. Within the impact area are seven targets for air-to-ground munitions delivery, two spotting towers, a scrap metal staging area, a road network between the targets, and range maintenance equipment. Most of the remaining acreage is vegetated, which effectively isolates the public from the impact area and provides a buffer for dropped munitions that may miss or ricochet away from the intended target.

Live and practice military munitions are employed at the Pinecastle Range. Six of the seven targets receive practice bombs only. The various practice bombs used at the range contain spotting charges to release smoke upon impact and do not contain high explosive filling. The use of live, explosive munitions, ranging from small rockets to 2000-pound bombs, is isolated to one target within the Live Impact Area (LIA).

4.1.5 What are the possible Navy sources (2009 Contaminant Site Use Summary - CSUS)?

Perchlorate is sometimes used in munitions fuses, smoke and flare rocket warheads, and possibly other components of some aerial bombs. However, as of the latest comprehensive range evaluation (CRE) performed for the Pinecastle Range Complex in 2009, no evidence was found indicating perchlorate was contained in munitions used at the range. Data collected during the Navy Range Sustainability Environmental Program Assessment (RSEPA) process indicates that since 1992 only 2.75- and 5-in rockets were used at the range. The motors of these air-launched rockets are nitrocellulose-and nitroglycerine based and do not contain perchlorates. No indications of the use of other types of rockets were discovered in the range databases.

The strafing target receives various calibers of non-explosive aircraft gun rounds. Both 7.62 and 0.50 caliber ball ammunition, which contain lead, have been fired on the strafe target at the range. In addition, 20 and 30-mm target practice projectiles, which are composed of 98% steel and 2% aluminum, are used on the strafe target. Removal of these projectiles was accomplished in 2005. No high explosives or incendiary devices are allowed in the strafing area.

Current procedures at the range prohibit burial of munitions for disposal. However, buried practice munitions from past range activities have been discovered on the range. On-range buried munitions sites are continuously sought by range operators and, when discovered, are exposed and the munitions moved to an on-range holding area for further initial demilitarization and recycling.

Before the range came under Navy control, the U.S. Army owned and operated the facility. Some munitions items expended during that time in the LIA may have contained perchlorate compounds. These items include practice and non-practice munition fuses, smoke and flare rocket warheads, and possibly other components of some aerial bombs, specifically,

- Fuze Bomb Nose FMU-95/B
- Fuze Incendiary M210
- Fuze Point Detonation M567
- Fuze Point Detonation M567 Delay with 0 Booster
- Fuze Point Detonation M568
- Fuze Point Detonation M935
- Fuze Point Detonation M936
- Fuze Smoke Pot M207A1
- Rocket Motor IGN MK165 Modification 0
- Warhead Flare 2.75-in Rocket M257
- Tracer MK14 modification 0

- Rocket Practice Smoke 2.751N with Warhead M274
- Infrared Flare Assembly MJU-23/B
- Infrared Flare Assembly MJU-23A1B
- Rocket Practice 2.75 in with Warhead M267 and Fuze M439
- Flare Aircraft Countermeasure M206
- Flare Aircraft Parachute MK24 Modification 2A with SUS BAND
- Flare Aircraft Parachute MK24 Modification 4 with AF Cable Modification
- Flare Aircraft Parachute MK45 Modification 0 with Drogue Tray
- Flare Aircraft Parachute MK45 Modification 0 with 0 Drogue Tray
- Flare Aircraft Parachute White MK45 Modification 0
- Flare Cartridge ALA-17B
- Warhead Flare 2.75-in Rocket M257
- Warhead Flare 2.75-in Rocket M278
- Cartridge 20MM 5 High Explosive Incendiary MK106/4 Armor-piercing Incendiary MK107/1 Armor-piercing with Tracer MK108
- Cartridge 20MM 9 Armor-piercing Incendiary MK107/1 Armor-piercing with Tracer MK108
- Cartridge 20MM Armor-piercing Incendiary M53
- Cartridge 20MMArmor-Piercing Incendiary MK107Modification 0
- Cartridge 20MMArmor-Piercing Incendiary MK107Modification 1
- Cartridge 20MMArmor-Piercing Incendiary T221 E2
- Cartridge 20MMHigh Explosive IncendiaryM56A1
- Cartridge 20MMMPT-5D M940
- Cartridge 20MMSAPHigh Explosive Incendiary PGU-28/B
- Cartridge 22MMSUBCAL Practice M744
- Cartridge 22MMSUBCAL Practice M745
- Cartridge 22MMSUBCAL Practice M746
- Cartridge 22MMSUBCAL Practice M747
- Cartridge 20MMHigh Explosive Incendiary M56A1
- Cartridge Caliber.504Armor-Piercing Incendiary MK211 Modification 0/1 Armor-Piercing Incendiary-TM20
- Cartridge Caliber.504Armor-Piercing Incendiary MK211 Modification 0/1 TracerM17
- Cartridge Caliber .50Armor-Piercing Incendiary MK211 Modification 0
- Cartridge Caliber .50 Blank Electric MK209 Modification 0
- Cartridge Caliber .50 Spotter Tracer M48A2

Although historical information on the Lake Bryant Range is limited, it is known that munitions impacted areas associated with the Lake Bryant Range do exist and that perchlorate may have been used during the training activities there. It has been suggested that this, combined with the close proximity to the Pinecastle Range Complex, could mean a potential munitions-related source may exist within the soil and groundwater of the impact area of the Range (NAVFACSE and EnSafe, 2009).

4.1.6 What are the possible natural sources?

Possible natural sources of perchlorate within the Pinecastle Range Complex include mineral deposits and atmospheric formation, as was described in Section 3.1.1. Chilean nitrate sources are not likely, as agricultural activities are not located on or near the range.

4.1.7 What are the possible non-Navy sources?

The major non-Navy anthropogenic sources of perchlorate are fireworks, road flares, perchloric acid and reagents manufacture, and chlorate or chlorine manufacture (GeoSyntec Consultants, 2005). These sources and others are generally described in Section 2.3. The potential of these sources to be present near the range

is likely low, but unknown. However, no industrial activity on the range has been documented and the only industry historically identified in the region adjacent to the range is possibly logging. The use of fireworks and road flares on or near the range is possible, but unlikely.

4.1.8 What are the Possible Pathways from the Above Sources?

4.1.8.1 Soil

The potential transport mechanisms for perchlorate, if present in soil, would be mobilization by water. The limiting factor for their vertical and horizontal movement is the soil's ability to be passed through by water. The sandy nature of the soil near the range makes it exceptionally well drained. Precipitation at the range infiltrates to the subsurface, as opposed to moving through overland drainage ditches. As water passes through, a portion of the perchlorate could be absorbed by the soil, with the remainder discharging to and diluting with shallow groundwater. The semi-confining clay layer, which underlies the surficial sand at the range, limits downward flow to deeper groundwater. Due to their potential to leach (drain) water to shallow groundwater near the range, impacted soils are considered a potential transport pathway.

4.1.8.2 Surface Water

No surface water bodies are located within 1 mi of the range. The nearest surface water body is Farles Lake, located more than 1 mi to the east of the range's boundary. Surface soils at the range are sandy in nature and drain immediately during times of precipitation. No surface water runoff exists at the range. Due to the absence of surface water features and surface water runoff near the range, surface water is not considered a potential transport pathway.

4.1.8.3 Groundwater

Shallow groundwater near the range is recharged primarily through infiltration of rain. Perchlorate that can reach a depth at which the soil is saturated may move horizontally in the preferred groundwater flow direction. Shallow groundwater at the range generally flows away from the target area and toward the south and east/southeast. Soil and shallow groundwater at the range are connected through infiltration, thus, groundwater is considered a potential transport pathway.

4.1.9 What Alteration Mechanisms Should I be Aware of? How Does This Affect Source ID?

At least three mechanisms can alter perchlorate: solubility, chemical oxidation/reduction, and biodegradation.

Perchlorate is a highly soluble, mobile ion that readily dissolves from inorganic salt ions in water. In addition, perchlorate does not sorb well to most surfaces (Urbansky, 2002). The four most common forms of perchlorate compounds found are ammonium perchlorate, sodium perchlorate, potassium perchlorate, and perchloric acid, all of which are easily transported in aqueous systems.

Perchlorate has a low charge density and does not generally form complexes with metals the way other anions do; however, it can be reduced by air-sensitive metal cations such as titanium(III) or ruthenium(II). These mechanisms are not generally present in natural systems, but can potentially be exploited in systems engineered for remedial purposes.

Perchlorate can be biodegraded in groundwater if perchlorate-degrading anaerobic bacteria are present, but only if significant levels of organic carbon are present, and if oxygen and nitrate are depleted. While it may be possible for these conditions to coexist at locations on the range, it is considered unlikely.

4.1.10 Co-Contaminants

The most common co-contaminants found at perchlorate-contaminated sites are nitrate and sulfate. Nitrate concentrations in contaminated media are generally far greater than those of perchlorate, and the presence of nitrate typically interferes with efficient reduction of the perchlorate anion. However, under reducing conditions nitrate is commonly removed along with perchlorate because most perchlorate-reducing bacteria are denitrifiers as well (Logan, 2001). The presence of sulfate should not adversely impact perchlorate

removal, as perchlorate is generally reduced before sulfate. However, if the redox potential is too low, sulfate may become the electron acceptor (ITRC, 2002).

The presence of co-contaminants at perchlorate sites also depends on facility-specific operations and historical practices. For example, most major weapons systems with solid propulsion, explosive devices, or pyrotechnic devices contain perchlorate compounds. At such sites, typical co-contaminants also include VOCs, halogenated VOCs such as trichloroethylene (TCE), solvents, and munitions constituents (MCs) such as 1,3,5-trinitrotoluene (TNT), royal demolition explosive, or cyclotrimethylenetrinitramine: 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), high-melting explosive or octagen: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and other MC-related compounds (ITRC, 2002). As part of the RSEPA monitoring program at Pinecastle Range, MCs and metals were quantified (NAVFAC Southeast and Aerostar Environmental Services, Inc., 2010). These data are summarized in Table 4-1.

Table 4-1. MCs and other analytes evaluated in groundwater at Pinecastle as part of the RCA in October 2010. Methods used were U.S. EPA SW846 Method 6010B (Metals) and U.S. EPA SW846 Method 8330A (MCs).

Analyte	MDL (µg/L)	Data Observed (µg/L)
Aluminum	25	ND, 2600, 976, 1440, 735
Arsenic	2	ND
Beryllium	1	ND
Cadmium	1	ND
Chromium	1	ND
Iron	35	ND, 2220, 353, 1440, 354, 682
Lead	1	ND
Manganese	1	ND, 82.9
Nickel	2	ND
Perchlorate	4	ND
Vanadium	1	ND
HMX	0.059	ND
RDX	0.069	ND, 0.59
1,3-dinitrobenzene	0.05	ND
2.6-dinitrotoluene	0.055	ND
2,4-dintrotoluene	0.05	ND
2-amino-4,6-dinitrotoluene	0.091	ND
4-amino-2,4,6-dinitrotoluene	0.082	ND
nitrobenzene	0.056	ND
o-nitrotoluene	0.086	ND
m-nitrotoluene	0.074	ND
p-nitrotoluene	0.067	ND
tetryl	0.051	ND
1,3,5-trinitrobenzene	0.05	ND
2,4,6-trinitrotoluene	0.052	ND
PETN	0.48	ND

4.2 SITE PERCHLORATE DATA AND DATA QUALITY EVALUATION

In December 2004, eight monitoring wells were installed in the surficial aquifer. The wells were at the range's western, southern, and eastern perimeter and along the east–west maintenance road, which crosses the range. The monitoring wells were identified as MW-5 through MW-9 and PZ-1 through PZ-3. Monitoring well locations are shown in Figure 4-3. To fill existing data gaps, six additional monitoring wells were installed at the range in August 2006. Monitoring wells MW-10 and MW-11 were installed topographically downgradient of the LIA of the range. Monitoring wells MW-12 and MW-13

(dry/abandoned, not shown) were positioned to confirm the presence of a hydrogeologic divide between the LIA and the northeastern boundary of the range. Monitoring wells MW-14 and MW-15 were installed to replace monitoring wells P-2 and P-1, critical wells that were covered over during forest road maintenance operations along the range perimeter.

From 2005–2010, groundwater samples were collected from 13 monitoring wells positioned around the range during four sampling events. Groundwater samples were also collected from two Forestry Service wells, located beyond the range boundaries, during the last two sampling events. In August 2006, surface soil samples were collected from six locations where precipitation could accumulate at the range. A map of the range showing wells and sampling locations is included as Figure 4-3. Groundwater and soil samples were tested for explosives, metals, and perchlorate, based on specific materials used during range operations.

Figure 4-3. Location of groundwater monitoring wells on the range. Map data: Image U.S. Geological Survey. ©2012 Google.

4.2.1 Analytical Chemistry Methods Used

From 2004–2009, perchlorate groundwater samples were obtained and analyzed for perchlorate via analytical method SW-846 Method 8321M/A (U.S. EPA, 1996). In 2006, soil samples were obtained and analyzed by analytical method SW-846 Method 8321A for perchlorate (U.S. EPA, 1996), as well as SW-846 Method 6010B for metals (U.S. EPA, 1996). Rapid screening tools (i.e., ion-selective electrode and colorimetry) were not used on the range because an approved monitoring program using conventional analytics is in place.

4.2.2 Perchlorate Data, Analysis, and Processing

Minimal concentrations of perchlorate were reported for 11 of 13 shallow monitoring wells at the range. However, similar concentrations of perchlorate were also measured in the range's production well and in the background well M-0411. No perchlorate concentrations reported during the 2004–2009 sampling events exceed the Florida Department of Environmental Protection (FDEP) Groundwater Cleanup Target Level (GCTL) of 4 µg/L or the Navy's perchlorate "level of concern" (per the May 2006 memo regarding perchlorate) of 24 µg/L.

A chronological summary of perchlorate data for groundwater on the range is shown in Figure 4-4 for samples collected from each of the monitoring wells shown in Figure 4-3. Note that there are no data for dry weels or those covered up by USFS road maintenance activities (PZ1, PZ2).
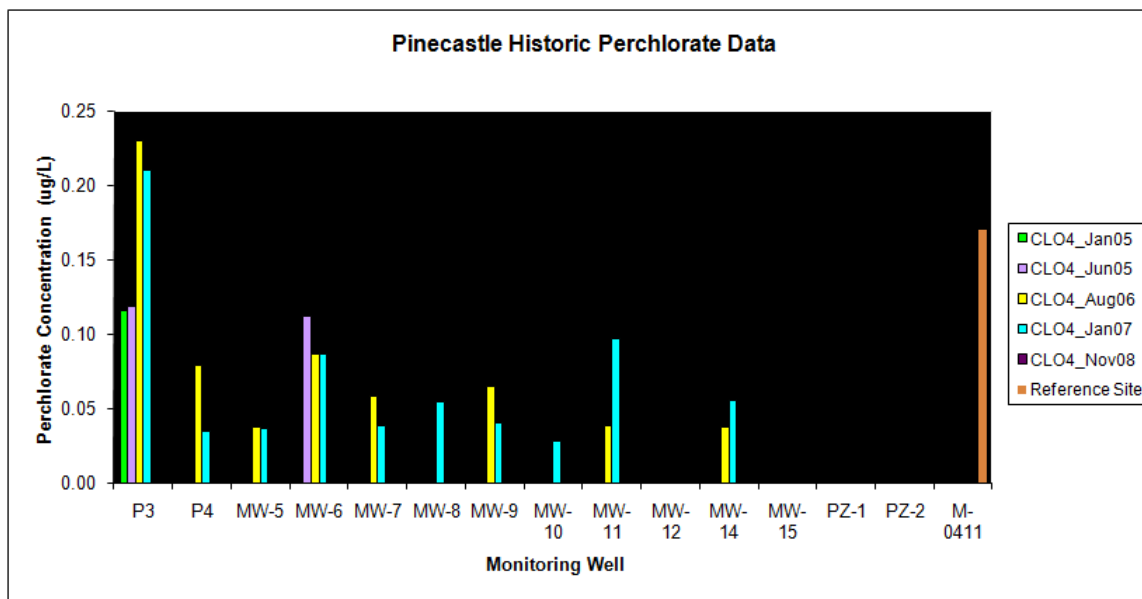

Figure 4-4. Documented occurrences of perchlorate in groundwater on the range from 2004–2009. The orange bar at the far right indicates the perchlorate concentration at the off-range reference site.

Note that in many cases the perchlorate concentrations were so low for equipment and method capabilities that the laboratory was forced to estimate the concentrations. Thus, a level of uncertainty exists about the actual amount present. Furthermore, perchlorate was reported at a concentration of 0.17 µg/L in the background well M-0411, more than 2.5 mi to the west from the Pinecastle boundary. The similar concentration at the background well indicates that even if perchlorate does exist in range groundwater, it may be naturally occurring or related to past use at the Lake Bryant Range.

Surface soil samples were collected from six locations positioned topographically down gradient from target areas, at preferred storm water runoff pathways and pooling areas within the range's boundary. Locations were selected based on results generated using the U.S. Army Corps of Engineers' Hydrologic Modeling System, a computer program designed to simulate the precipitation runoff and routing processes of dendritic watershed systems. Surface soil sampling was performed in accordance with Florida Department of Environmental Protection (FDEP) Standard Operating Procedure (SOP) FS 3000 and applicable planning documents. Soil stratigraphy was notably different in the southwest corner of the range at well locations MW-8 and MW-9. At MW-8, inter-bedded medium to fine and coarse to medium sand was present from the ground surface to a depth of 135 ft bgs, where the boring was terminated. The absence of a clay unit at depth suggests the Hawthorne Group is laterally discontinuous or has been breached near MW-8. In stark contrast with MW-8, a medium to fine grain sand was only encountered to a depth of approximately 10 ft bgs at MW-9 before grading to sandy clay that, with the exception of a few minor sand stringers, was continuous to

75 ft bgs, the terminal depth of the boring (NAVFAC SE and EnSafe, 2009). Perchlorate was not detected in the six surface soil samples collected at the range in 2006. This is consistent with the CSUS finding of no documented perchlorate use on the range.

In 2010 and in 2012, groundwater samples were collected separately as part of this developmental case study and analyzed at a lower detection limit for perchlorate as part of the advanced chemical analysis effort described below in Section 4.3.

4.2.3 Conclusion based on CSM, CSUS, and Existing Perchlorate Data

The lack of identifiable perchlorate uses on the range, combined with the presence of a low-level perchlorate signature in groundwater are sufficient to justify the need for further investigation incorporating forensic approaches. Using forensic approaches will make it possible to evaluate the potential nature (synthetic vs. natural) of the source of perchlorate in groundwater.

4.3 ADVANCED CHEMICAL ANALYSIS

4.3.1 Forensic Sampling and Analysis of Correlation Analytes

In Table 2-4, a range of environmental data and other analytes were described that appear to be correlated with various synthetic or natural perchlorate sources. The evaluation of a selection of these correlation analytes was considered a starting point for potential source identification in the groundwater on the range. Such information can provide valuable clues as to where (spatially) the perchlorate signature might be coming from on the range and what types of advanced methodologies and strategies would best be employed for extended studies focused on specific or unique perchlorate sources. A selection of potential correlation analytes evaluated as part of the case study for Pinecastle Range is shown in Table 4–2. These analytes are unregulated and not quantified as part of the existing sampling and analysis under the RCA/RSEPA program. Thus, data quality objectives and sampling for these analytes were incorporated into planned 2010 and 2012 range assessment activities as described in Section 4.3.2.

4.3.2 Range Sampling

During October 2010 and October 2012, groundwater sampling was performed in accordance with the FDEP SOP Florida Statute 2200. A typical monitoring well is shown in Figure 4-5 (from the 2010 Pinecastle Range sampling event). Well purging and sampling were conducted using a bladder pump, equipped with a check valve to prevent backflow, and dedicated polyethylene tubing (see Figure 4-6). A minimum of one well volume was purged from each well prior to collecting stabilization parameters. Whenever possible, the purge flow was adjusted to minimize drawdown in the well and reduce hydraulic stress on the formation. A multi-parameter probe, equipped with a flow-through cell, was used to measure groundwater parameters. Parameters were recorded in 2- to 3-min intervals during purging. Purging was performed until parameters were deemed stable per FDEP guidance or until the well was purged dry.

If the well was purged dry, sampling was performed after allowing sufficient well recovery and within 6 hours of the initial purge event, per FDEP SOPs. Monitor wells PZ-1, PZ-3, and MW-15 were dry during the 2010 sampling event, and during the October 2012 sampling event, PZ-1 and PZ-3 were dry, while MW-15 and P4 contained insufficient water volume; therefore, groundwater sampling was not possible at these wells.

Following well purging, groundwater samples were collected from monitor wells P3, P4 (2012 only), MW-5, MW-6, MW-7, MW-8, MW-9, MW-10, MW-11, MW-12, MW-14, and PZ-2. Samples were collected directly into laboratory-supplied bottles and were submitted for laboratory analysis. Groundwater samples collected during the sampling events were submitted to Accutest Laboratories in Orlando, Florida, for analysis of a standard suite of analytes as part of the Pinecastle Groundwater Monitoring program. The analyte list for groundwater samples included explosives and perchlorate (SW-846 method 8321M/A) and metals (SW-846 Method 6010B). These analytes reflect the RSEPA requirements and accounts for the site-specific considerations related to the operational history of the Range. For correlation analytes specific to this case study, samples were submitted to TestAmerica Laboratories in Savannah, Georgia, and Denver, Colorado; Columbia Analytical Laboratories (ALS) in Jacksonville, Florida; and Applied Speciation and

Consulting Laboratories in Jacksonville, Florida for the various correlation analytes, either not regulated/quantified under RSEPA, or for quantitation at lower detection levels required for environmental forensics.

Table 4-2. Groundwater correlation analytes using ion chromatography (IC), inductively coupled plasma absorption emission (ICP-AE) evaluated at Pinecastle Range for potential association with perchlorate. Perchlorate analysis is also indicated, as it was measured concurrently in the samples at a lower quantitation level using ICP tandem mass spectrometry (ICP-MS/MS).

Correlation analyte	Method	Target MDL (mg/L)	References
Nitrate (NO_3^-)	IC	0.01	Appendix A, USEPA 300.1 Rev 1.0
Nitrite (NO_2^-)	IC	0.01	Appendix A, USEPA 300.1 Rev 1.0
Chloride (Cl^-)	IC	0.02	Appendix A, USEPA 300.1 Rev 1.0
Sulfate (SO_4^{2-})	IC	0.02	Appendix A, USEPA 300.1 Rev 1.0
Iodide (I^-)	IC	0.5, required MDL study	Appendix A, USEPA 300.1 Rev 1.0
Iodate (IO_3^-)	IC	0.5, required MDL study	Appendix A, USEPA 300.1 Rev 1.0
Magnesium (Mg)	ICP-AE	0.02	USEPA 200.7 Rev 4.4
Iron (Fe)	ICP-AE	0.03	USEPA 200.7 Rev 4.44
Calcium (Ca)	ICP-AE	0.01	USEPA 200.7 Rev 4.4
Sodium (Na)	ICP-AE	0.03	USEPA 200.7 Rev 4.4
Perchlorate (ClO_4^-)	ICP MS/MS	0.00002	USEPA 6860

All samples were received by the subcontracted laboratory intact, under chain-of-custody documentation, and within proper temperature guidelines. The equipment blank was chemically presevered for metals upon laboratory receipt. All other samples were preserved in the field according to respective method guidelines. Hold-time requirements were met for all samples analyzed. Field duplicates were collected from MW-10 during the October 2010 sampling and from MW-11 during the October 2012 sampling. Results of the laboratory analyses showed matrix spike (MS)/matrix spike duplicate (MSD) recoveries within QC limits for all fractions.

For the October 2010 and 2012 sampling events, the required detection limit for perchlorate was lower, which required an extra filtration step (Figure 4.7). The initial detection limit under the RSEPA groundwater monitoring was 4.0 µg/L per EPA Method 314. In this effort, the detection limit was lowered to 0.05 µg/L by EPA Method 6860 (SW-846).

Figure 4-5. Typical monitoring well on the Pinecastle Range.

Figure 4-6. The well purging process.

Figure 4-7. Filtering the sample for perchlorate analysis.

4.3.3 Sample Data, Analysis, and Interpretation

The data for analytes listed in Table 4-2 are summarized separately for the 2010 and 2012 sampling events. Associated sample information and analyte data in the table were evaluated for use in correlation analyses. Data are not included for dry wells, and data are only included for those samples in which any given analyte was detected in four or more wells ($N \geq 4$). For example, NO_2^- was never detected in 2010 and is not included in the dataset, but seven samples had quantifiable Fe, thus data for those samples are included in the dataset, while the remaining five samples were considered non-detect (ND) and values were not estimated for purposes of subsequent statistical and correlation analyses.

4.3.4 October 2010 Data, Analysis, and Interpretation

Data summarized in Table 4-3 were evaluated and used for inter-correlation analyses between variables.

Correlation analyses were only performed for data on samples with quantified values. If a variable (analyte) was ND, that sample data was not included in the correlation dataset. If a large number of NDs were observed for a given analyte resulting in a greatly reduced N (reduced statistical confidence), that analyte was not included in the primary correlation dataset for subsequent principal components analysis (PCA), and a separate simple correlation analysis was performed on samples with detections of that variable, due to the limited statistical confidence. Additionally, when a data value in a given sample was observed as a statistical outlier during preliminary linear correlations (discreet pairwise variable comparisons) and verified with subsequent statistical outlier analyses, that sample data was not included in the correlation dataset. The latter (outlier) scenario was observed to occur in only one sample for NO_3^- (1.1 mg/L in sample MW-10), whereas the former (many NDs) scenario occurred for two analytes; NDs were present in four samples for Fe and eight samples for Al. For either the ND or outlier case, the statistical confidence was decreased (N was reduced) for those correlation analyses, and reported correlation coefficients were valid only for those N

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associated samples. These were evaluated on a case-by-case basis to determine if a PCA should be performed.

Table 4-3. Simple statistics of correlation analyte data for samples collected at Pinecastle Range (October 2010). TDS is total dissolved solids.

Variable	N	Mean	Std. Dev.	Sum	Minimum	Maximum
ClO_4^- (mg/L)	12	0.000145	0.000246	0.001737	0.000016	0.00091
Specific Conductivity (µmhos/cm)	12	31.500	18.228	378	17	81
NO_3^- (mg/L)	12	0.233	0.340	2.8	0.03	1.1
Cl (mg/L)	12	3.792	2.175	45.5	1.3	7.8
SO_4^{2-} (mg/L)	12	3.317	6.242	39.8	0.56	23.0
TDS (mg/L)	12	25.500	13.575	306	8	53
Ca (mg/L)	12	0.879	1.095	10.55	0.13	3.5
Mg (mg/L)	12	0.507	0.194	6.08	0.26	1.0
Na (mg/L)	12	3.069	3.003	36.83	0.95	12.0
Fe (mg/L)	8	0.516	0.662	4.13	0.04	2.00
Al (mg/L)	4	1.438	0.828	5.751	0.735	2.600
GW Elevation (feet above mean sea level)	12	54.550	18.098	654.6	38.32	90.82
pH	12	5.231	0.598	62.77	4.2	6.42
Temperature (Celsius)	12	24.558	1.970	294.7	21.8	28.9
Dissolved Oxygen (mg/L)	12	6.949	1.530	83.39	4.07	10.9
Turbidity (NTUs)	12	14.858	4.258	178.3	10.6	25.4

Correlation results are presented as correlation matrices on Table 4-4, Table 4-5, and Table 4-6 for the primary dataset (not including Fe or Al as variables, or sample MW-10, with the NO_3^- outlier). In these correlation analyses, it was observed that in some cases that correlation between some of the variables was insignificant. These variables were removed from the correlation dataset to further reduce the dimensionality of the dataset before performing PCA, *i.e.* thus including only those variables that exhibit one or more significant correlations with another variable. These results are summarized in Table for the dataset with the largest statistical confidence (N = 11).

Table 4-4. Correlation matrix for analytes in samples with highest statistical confidence (N = 11) for 2010 sample data summarized in Table 4–3, subsequent to dataset robustness evaluation including outlier analysis. Significant correlations (p < 0.05) are shown in **bold italics**. These data were sufficiently robust for further analysis using principal components analysis (PCA) as described in the text.

	ClO4	Spec. Cond.	NO3	Cl	SO4	TDS	Ca	Mg	Na	GW Elev.	pH	Temp	DO	Turbidity
ClO4	1.0000													
Specific Cond	*0.8386*	1.0000												
NO3	*0.9697*	*0.7535*	1.0000											
Cl	-0.0482	0.4095	-0.1859	1.0000										
SO4	*0.9762*	*0.8278*	*0.9587*	-0.0985	1.0000									
TDS	0.4794	*0.7658*	0.3789	0.5123	0.4166	1.0000								
Ca	-0.2230	0.1968	-0.2656	0.3733	-0.2548	0.5452	1.0000							
Mg	-0.0341	0.3415	-0.0726	0.4584	-0.0525	*0.6892*	0.7138	1.0000						
Na	*0.9445*	*0.9431*	*0.8777*	0.2590	*0.9238*	*0.6074*	-0.1085	0.0681	1.0000					
GW Elev.	0.5074	0.2465	*0.6713*	-0.3773	0.5579	-0.1889	-0.3935	-0.3070	0.3917	1.0000				
pH	0.3207	0.2256	0.4711	-0.4006	0.3553	0.0893	0.2120	0.2114	0.1708	*0.7218*	1.0000			
Temp	0.2572	0.2737	0.2250	-0.2806	0.3775	0.2574	0.1074	0.2138	0.1782	0.0790	0.3849	1.0000		
DO	0.1443	-0.1892	0.2175	-0.4797	0.0321	0.1227	-0.1839	-0.0303	-0.0535	0.0424	0.0981	-0.1202	1.0000	
Turbidity	*0.8131*	0.5585	*0.7817*	-0.4047	*0.8263*	0.2998	-0.2064	-0.0082	*0.6349*	0.3213	0.3709	0.5891	0.2292	1.0000

Table 4-5. Correlation matrix for samples with Fe detections for 2010 sample data summarized in Table 4-3, subsequent to dataset robustness evaluation including outlier analysis as described in the text. Note that while the dataset is reasonably robust for samples with Fe detected, the statistical confidence is much lower (N = 7). Significant correlations (p < 0.05) are shown in **bold italics**.
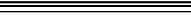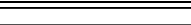
	ClO4	Specific Cond.	NO3	Cl	SO4	TDS	Ca	Mg	Na	GW Elev.	pH	Temp	DO	Turbidity	Fe
ClO4	1.0000														
Specific Cond	-0.2153	1.0000													
NO3	*0.9291*	-0.3121	1.0000												
Cl	-0.1312	*0.9121*	-0.2350	1.0000											
SO4	0.0220	-0.6728	0.0594	-0.4738	1.0000										
TDS	0.1240	*0.8998*	0.0243	*0.7789*	-0.5862	1.0000									
Ca	-0.2673	*0.7508*	-0.2794	0.4204	*-0.7928*	*0.7232*	1.0000								
Mg	-0.0671	*0.7978*	-0.1231	0.6037	-0.3974	*0.8634*	*0.7631*	1.0000							
Na	0.2146	0.7359	0.1084	*0.9160*	-0.4256	0.6842	0.1811	0.3907	1.0000						
GW Elev.	0.2366	-0.6589	0.3219	-0.4017	*0.8305*	-0.4989	*-0.8409*	-0.5813	-0.2150	1.0000					
pH	-0.0482	0.2761	-0.0825	-0.1115	-0.3371	0.4693	0.7409	0.5953	-0.3110	-0.4420	1.0000				
Temp	-0.4889	-0.0955	-0.5718	-0.2718	0.3473	-0.0625	0.1212	0.1047	-0.5343	0.1336	0.5406	1.0000			
DO	*0.9645*	-0.4030	0.9635	-0.3447	0.1648	-0.0355	-0.3366	-0.1498	-0.0088	0.3522	-0.0055	-0.4081	1.0000		
Turbidity	0.2151	-0.6957	0.2699	*-0.8646*	0.5014	-0.4216	-0.2066	-0.2093	*-0.8481*	0.3793	0.4654	0.5149	0.4192	1.0000	
Fe	*0.8335*	-0.1697	0.7524	-0.2206	0.1073	0.1711	-0.0573	0.2539	-0.0304	0.0215	0.2670	-0.2309	*0.8472*	0.4391	1.0000

Table 4-6. Principal components analysis (PCA) to explore the interdependencies summarized in the 2010 data correlation matrix in Table 4-4 (N = 11). Prior to performing the PCA, the dimensionality of the dataset (number of dependent variables or analytes) was first reduced, as described in the text, by excluding variables that did not show any significant correlation in Table 4-4. PCA results are also shown graphically in Figure 4-8, Figure 4-9. and Figure 4-10.

Correlation Matrix

	ClO4	Spec. Cond.	NO3	SO4	TDS	Ca	Mg	Na	GW Elev.	pH	Turbidity
ClO4	1										
Specific Conduct.	0.8386422	1									
NO3	0.96967804	0.75347421	1								
SO4	0.97619616	0.8277752	0.95865623	1							
TDS	0.4793749	0.76575491	0.37892268	0.41655968	1						
Ca	-0.223015	0.19678617	-0.2656232	-0.2547898	0.54523225	1					
Mg	-0.0341407	0.34145476	-0.0726422	-0.0525412	0.68918619	0.71380341	1				
Na	0.94451928	0.94309339	0.87770949	0.92376694	0.60737845	-0.1084727	0.06808214	1			
GW Elev.	0.5074036	0.24651705	0.6712942	0.55792831	-0.1889461	-0.3934883	-0.3069767	0.3916974	1		
pH	0.32074585	0.22556353	0.47108196	0.35528303	0.08926725	0.21200042	0.21137469	0.17081907	0.7217865	1	
Turbidity	0.81313371	0.55853054	0.78167354	0.82632662	0.29983284	-0.2064349	-0.0082041	0.63488974	0.32126906	0.37090168	1

Explained Variance (Eigenvalues):

Number	Eigenvalue	Percent	Percent	Cum Percent
1	5.9653	54.230		54.230
2	2.6831	24.391		78.622
3	1.3885	12.623		91.244
4	0.5205	4.732		95.976
5	0.2713	2.466		98.442
6	0.1114	1.013		99.455
7	0.0388	0.353		99.808
8	0.0161	0.146		99.954
9	0.0034	0.031		99.985
10	0.0016	0.015		100.000

Component Score Coefficients (Eigenvectors):

| Variable	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11
ClO4	0.40182	-0.04929	-0.11827	0.03121	0.05437	-0.10339	0.36383	-0.40348	-0.05773	0.62341	-0.34693
Specific Conductance	0.35840	0.23094	-0.13033	-0.27205	0.10327	0.43883	-0.29391	-0.17934	-0.15635	-0.38679	-0.48102
NO3	0.39683	-0.11344	0.03543	-0.01685	-0.03034	-0.25382	0.63194	0.20532	-0.19029	-0.53301	0.03084
SO4	0.40068	-0.07868	-0.08240	0.04888	0.02124	0.22431	-0.19992	0.66395	-0.36684	0.35950	0.16942
TDS	0.21852	0.48190	-0.11831	-0.09558	-0.09271	-0.73718	-0.35161	0.11101	0.06445	0.01054	-0.06810
Ca	-0.04920	0.52928	0.27784	-0.02333	0.66759	0.12671	0.27272	0.21115	0.22146	0.09823	0.01796
Mg	0.03343	0.53852	0.20949	0.12680	-0.70255	0.29928	0.22892	0.03298	0.06520	0.08075	0.03889
Na	0.38377	0.05380	-0.21813	-0.28776	0.04209	0.13893	-0.02802	-0.31503	0.27451	-0.01042	0.72311
GW Elevation	0.22912	-0.33856	0.45967	-0.38538	-0.15271	-0.01180	-0.08269	0.22968	0.57944	0.07042	-0.22205
pH	0.18282	-0.02196	0.75191	0.11800	0.07462	-0.09904	-0.23223	-0.33412	-0.40987	-0.01655	0.19387
Turbidity	0.32801	-0.06936	-0.04074	0.80706	0.08066	0.06076	-0.17308	-0.02050	0.40606	-0.16366	-0.04855

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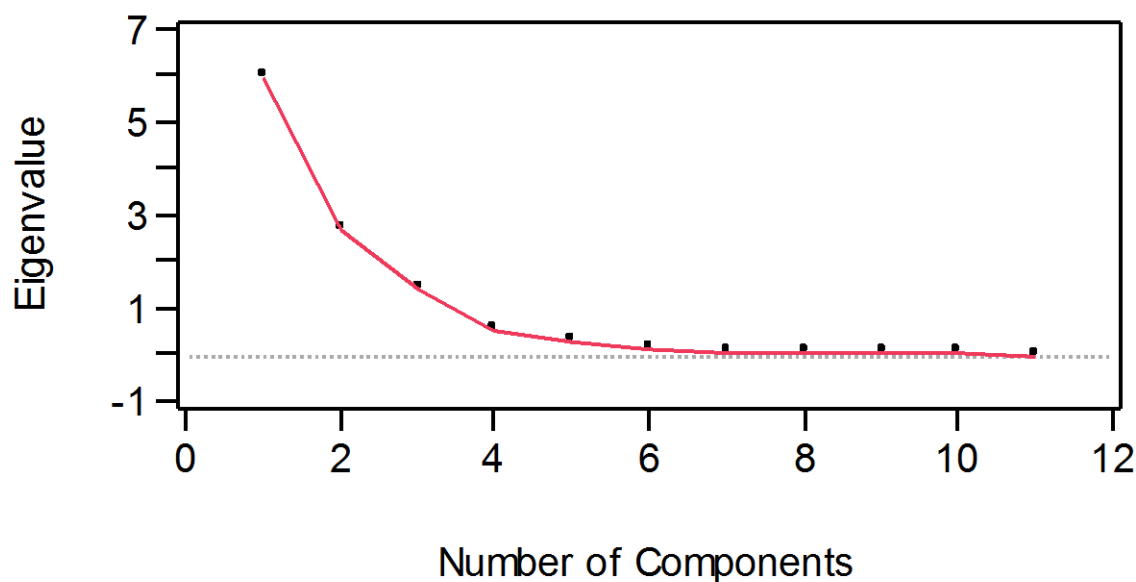
Figure 4-8. Plot showing the relationship between the primary PCs and how they account for the 2010 dataset variability in the PCA evaluation shown in Table 4-6.
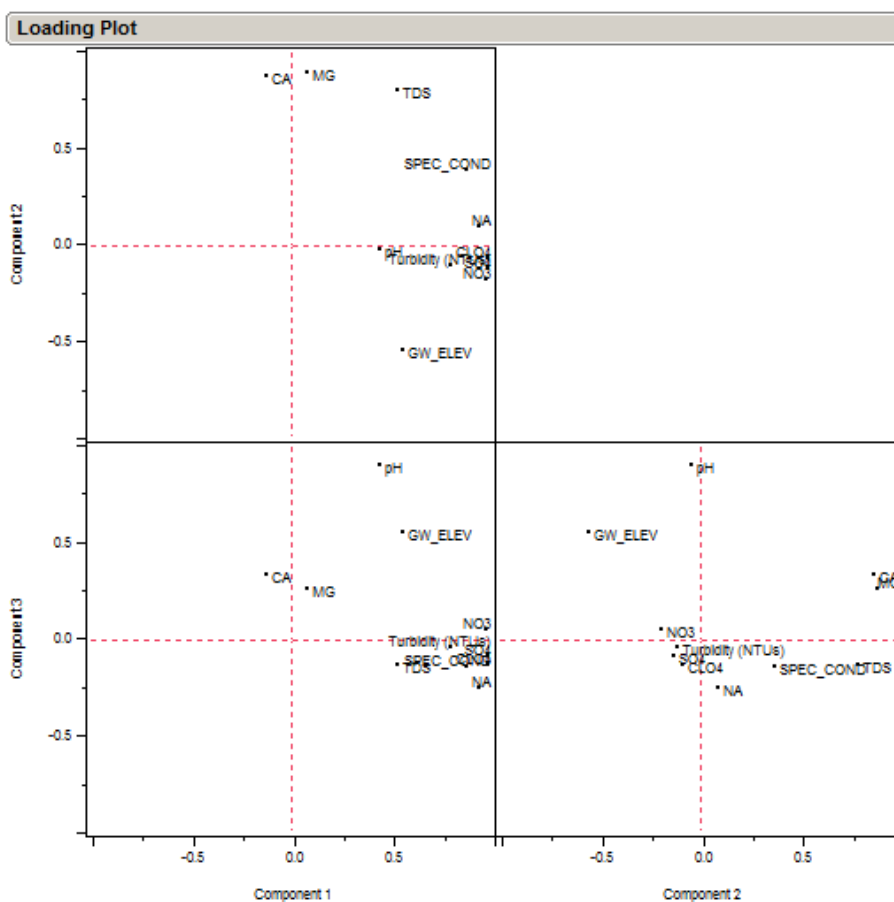

Figure 4-9. Loading plots showing the relationship between the primary principal components PCs (accounting for > 90% of the dataset variability) and 2010 analysis variables for the PCA evaluation shown in Table 4-6.
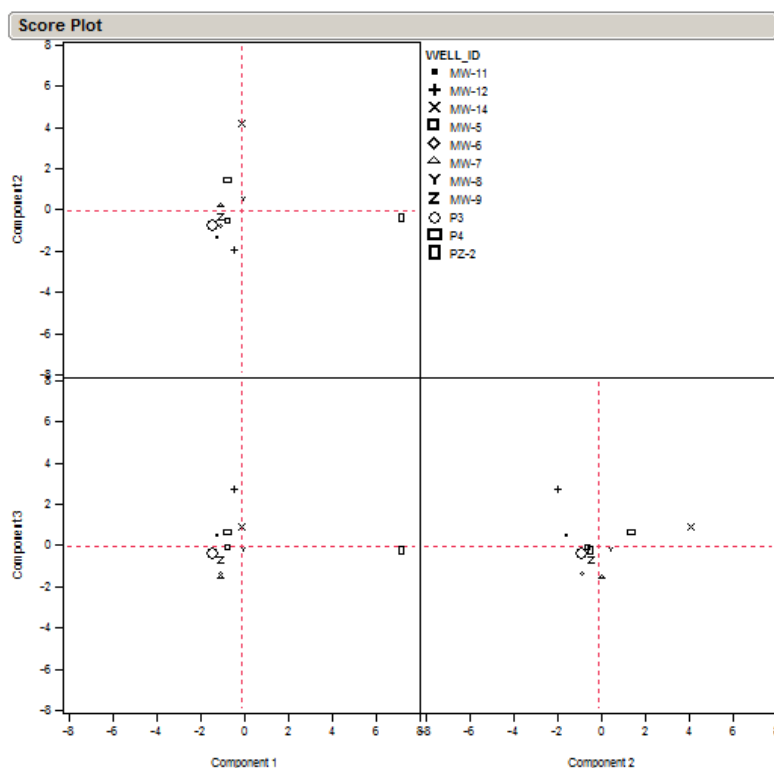
Figure 4-10. Score plots showing the relationship between the primary principal components PCs (accounting for > 90% of the dataset variability) and 2010 groundwater monitoring wells for the PCA evaluation shown in Table 4-6.

4.3.5 October 2012 Sample Data, Analysis, and Interpretation

The data for analytes listed in Table 4–2 are summarized below for the 2012 sampling event. As for the 2010 data treatment, data are not included for dry wells, and data are only included for those samples in which any given analyte was detected in four or more wells (N ≥ 4). There are two differences noted for sample analyses in 2012: TDS was not quantified and IO_4 analyses were performed at lower detection limits than 2010. The presence of Fe was again not observed in all of the samples, resulting in a decreased statistical confidence for correlations with Fe in the dataset (N=9).

Data summarized below (Table 4-7) were evaluated and used for inter-correlation analyses between variables. Note that N decreased slightly due to no sampling of a monitoring well that went dry but was not dry in 2010, but increased slightly for wells with quantified Fe.

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Table 4-7. Simple statistics of correlation analyte data for samples (N $\geq$ 4) collected at Pinecastle Range (October 2012).

Variable	N	Mean	Std. Dev.	Sum	Minimum	Maximum
ClO_4^- (mg/L)	11	0.00012482	0.00013331	0.001373	0.000014	0.00048
Specific Conductivity (µmhos/cm)	11	28.9090909	19.9622371	318	13	81
NO_3^- (mg/L)	11	0.324	0.35690083	3.564	0.06	1.1
Cl (mg/L)	11	3.65454545	2.21149887	40.2	1.1	6.6
SO_4^{2-} (mg/L)	11	5.17	8.80825181	56.87	0.97	31
Ca (mg/L)	11	0.80272727	1.06586201	8.83	0.16	3.9
Mg (mg/L)	11	0.52363636	0.23243376	5.76	0.24	1.1
Na (mg/L)	11	3.97909091	4.8252885	43.77	0.92	18
Fe (mg/L)	9	2.08711111	4.15961478	18.784	0.034	13
GW Elevation (feet above mean sea level)	11	53.8754545	18.5342156	592.63	38	86.75
pH	11	5.24545455	0.4392121	57.7	4.83	6.14
Temperature (Celsius)	11	24.3181818	1.3541183	267.5	22.7	28.1
Dissolved Oxygen (mg/L)	11	5.63181818	1.5598001	61.95	3.51	7.87
Turbidity (NTUs)	11	17.3727273	6.73068955	191.1	2.6	28.4
IO_4^- (mg/L)	11	0.00367182	0.0017336	0.04039	0.00049	0.00602

Table 4-8. Correlation matrix for analytes in samples with highest statistical confidence (N = 10) for 2012 sample data summarized in Table 4-7, subsequent to dataset robustness evaluation including outlier analysis. Significant correlations ($p < 0.05$) are shown in ***bold italics***. These data were sufficiently robust for further analysis using principal components analysis (PCA) as described in the text.
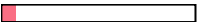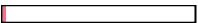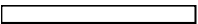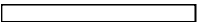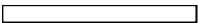
	ClO4	Specific Cond.	NO3	Cl	SO4	Ca	Mg	Na	GW_ELEV	pH	Temp	DO	Turbidity)	IO4
ClO4	1.0000													
Specific Cond	*0.7899*	1.0000												
NO3	*0.7935*	0.5429	1.0000											
Cl	0.0062	0.5380	-0.3002	1.0000										
SO4	*0.9423*	*0.8592*	*0.7828*	0.1112	1.0000									
Ca	-0.1417	0.2468	-0.1500	0.3552	-0.1659	1.0000								
Mg	-0.1892	0.1718	-0.0780	0.2314	-0.1854	*0.8866*	1.0000							
Na	*0.8922*	*0.9433*	*0.6664*	*0.3669*	*0.9604*	-0.0551	-0.1369	1.0000						
GW_ELEV	0.3809	0.2769	0.6141	-0.1394	0.5127	-0.3078	-0.3794	0.4614	1.0000					
pH	0.2080	0.3012	0.3199	-0.0249	0.0962	*0.8065*	*0.6974*	0.1172	-0.1104	1.0000				
Temp	-0.0959	-0.2473	-0.0490	-0.4003	-0.0622	-0.1295	0.0516	-0.2320	-0.0386	-0.1869	1.0000			
DO	0.1550	0.2086	-0.1391	0.2628	-0.0497	0.5271	0.3302	0.0575	-0.3593	0.4471	-0.4995	1.0000		
Turbidity	0.0091	-0.0171	-0.0500	-0.1649	-0.0723	0.2713	0.5166	-0.1725	-0.5669	0.1506	0.4212	0.2699	1.0000	
IO4	0.2504	0.3702	-0.0579	0.3942	0.2515	0.1683	0.0119	0.3418	0.3127	0.0092	0.0055	0.2578	-0.3123	1.0000

Table 4-9. Principal components analysis (PCA) to explore the interdependencies summarized in the 2012 data correlation matrix in Table 4.8 (N = 10). Prior to performing the PCA, the dimensionality of the dataset (number of dependent variables or analytes) was first reduced, as described in the text, by excluding variables that did not show any significant correlation in Table 4-8. PCA results are also shown graphically in Figure 4-11, Figure 4-12, and Figure 4-13.

Correlation Matrix

	ClO4	Specific Cond.	NO3	SO4	Ca	Mg	Na	pH
CLO4	1.0000	0.7899	0.7935	0.9423	-0.1417	-0.1892	0.8922	0.2080
SPEC_COND	0.7899	1.0000	0.5429	0.8592	0.2468	0.1718	0.9433	0.3012
NO3	0.7935	0.5429	1.0000	0.7828	-0.1500	-0.0780	0.6664	0.3199
SO4	0.9423	0.8592	0.7828	1.0000	-0.1659	-0.1854	0.9604	0.0962
CA	-0.1417	0.2468	-0.1500	-0.1659	1.0000	0.8866	-0.0551	0.8065
MG	-0.1892	0.1718	-0.0780	-0.1854	0.8866	1.0000	-0.1369	0.6974
NA	0.8922	0.9433	0.6664	0.9604	-0.0551	-0.1369	1.0000	0.1172
pH	0.2080	0.3012	0.3199	0.0962	0.8065	0.6974	0.1172	1.0000

Explained Variance (Eigenvalues):

Number	Eigenvalue	Percent	Percent	Cum Percent
1	4.3536	54.420		54.420
2	2.6747	33.434		87.854
3	0.6300	7.875		95.729
4	0.2196	2.746		98.475
5	0.0830	1.038		99.512
6	0.0220	0.275		99.787
7	0.0165	0.207		99.994
8	0.0005	0.006		100.000

Component Score Coefficients (Eigenvectors):

| Variable	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
ClO4	0.45925	-0.06176	0.11207	-0.24543	0.76291	-0.08829	0.34448	0.06323
Specific Cond	0.42979	0.14026	-0.46403	0.03956	-0.19924	-0.40394	0.08058	-0.60774
NO3	0.39281	-0.01862	0.66682	0.39780	-0.35606	-0.00053	0.33669	-0.04803
SO4	0.46940	-0.08644	-0.06940	0.11249	0.07398	0.68910	-0.49359	-0.17539
Ca	-0.01637	0.59680	-0.19314	-0.21621	-0.16462	0.50626	0.52341	0.04642
Mg	-0.03665	0.57257	-0.08354	0.68119	0.34758	-0.14069	-0.17321	0.17095
Na	0.46162	-0.04009	-0.30427	-0.06578	-0.30492	-0.17081	-0.07638	0.74861
pH	0.12260	0.53206	0.43102	-0.50221	-0.07174	-0.22115	-0.45613	-0.04226
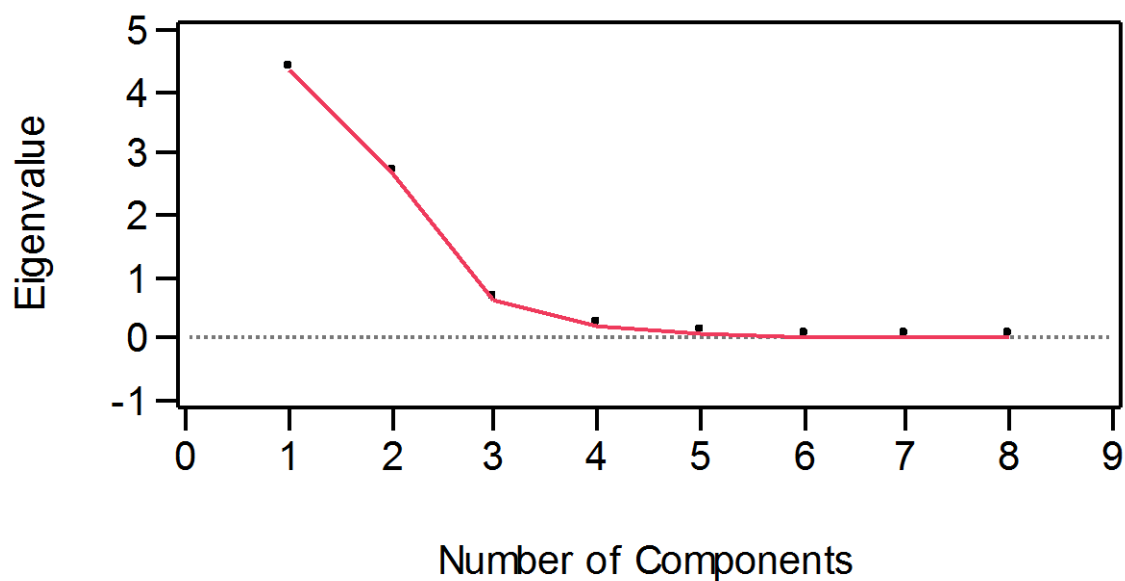
Figure 4-11. Plot showing the relationship between the primary PCs and how they account for the 2012 dataset variability in the PCA evaluation shown in Table 4-9.
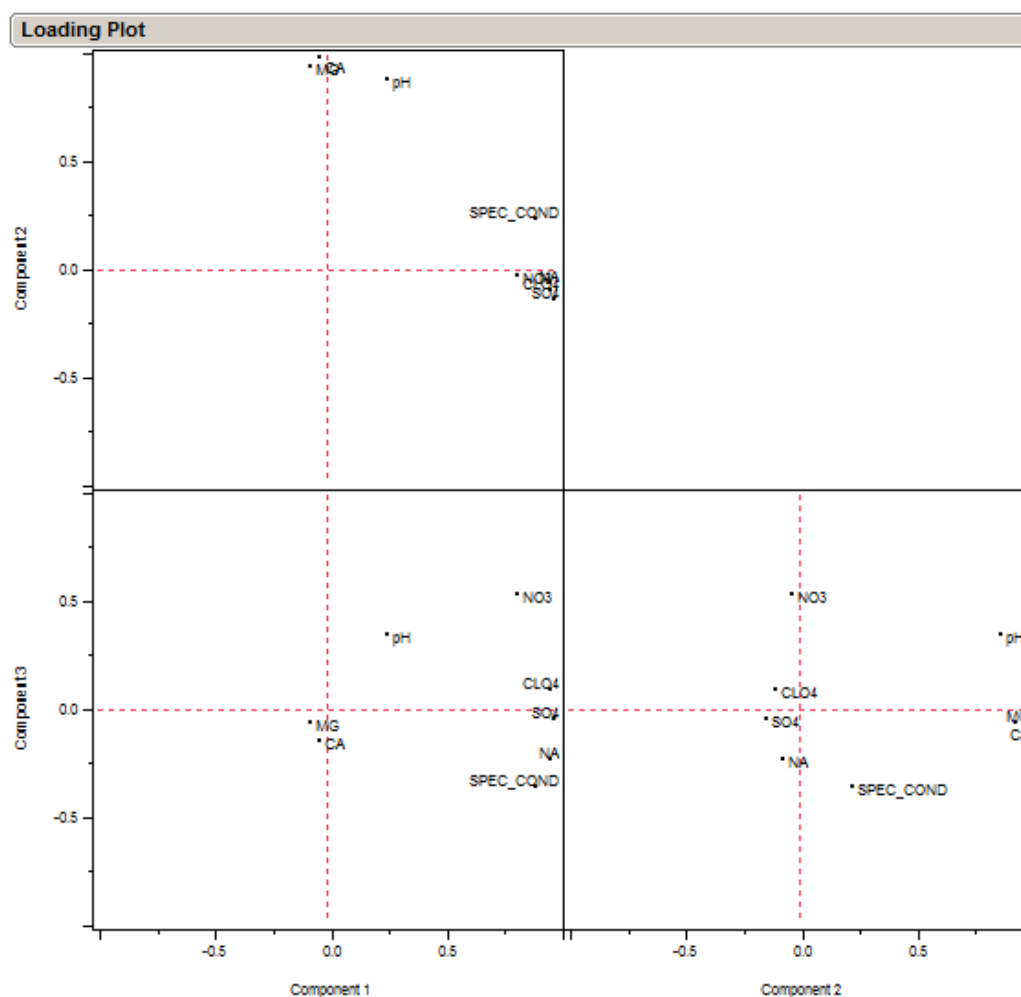

Figure 4-12. Loading plots showing the relationship between the primary principal components PCs (accounting for > 90% of the dataset variability) and 2012 analysis variables for the 2012 PCA evaluation shown in Table 4-9.
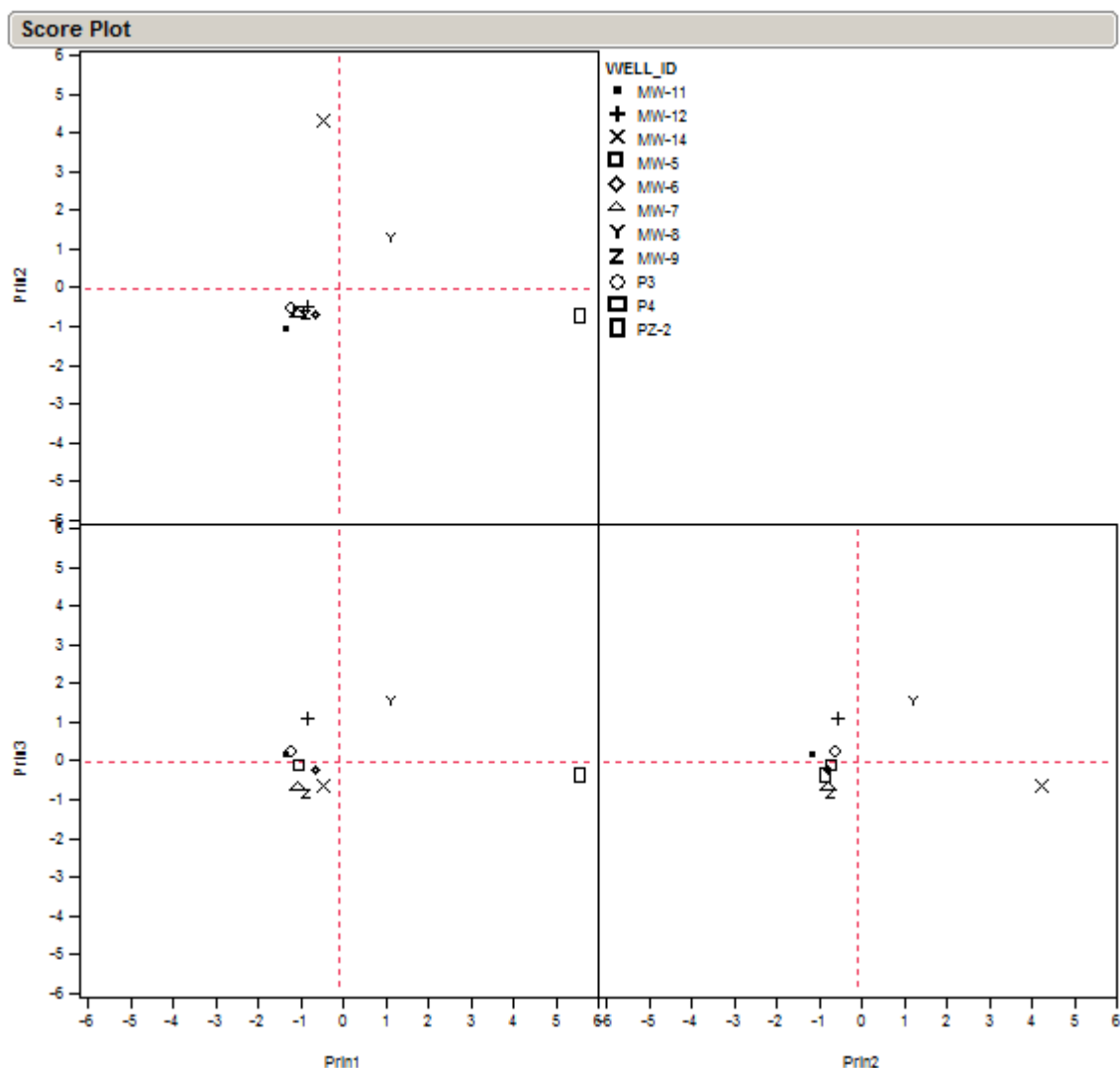
Figure 4-13. Score plots showing the relationship between the primary principal components PCs (accounting for > 90% of the dataset variability) and 2012 groundwater monitoring wells for the PCA evaluation shown in Table 4-9.

4.4 PINECASTLE CASE STUDY – SUMMARY AND DISCUSSION

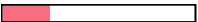### 4.4.1 Comparison of October 2010 and 2012 Correlation Results
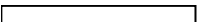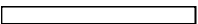
Data for analytes listed in Table 4-2 that were detected in both 2010 and 2012 sampling events were compared to evaluate spatial consistency and reproducibility. A general observation when comparing the simple correlations for both datasets is that there was less correlation overall among the variables in the 2012 data. To do a quantitative comparison, the data analysis must consider this by including only those variables common to both the 2010 and 2012 datasets. For simplicity, the 2010 dataset comprising only the variables and statistical confidence (N = 10) associated with or defined by the 2012 data analysis described above was evaluated, and hereafter referred to as the 2010 comparison dataset. Using this approach, the 2012 results above (Table 4-9 and Figure 4-11, Figure 4-12, and Figure 4-13) can thus be compared directly with the results for the 2010 comparison dataset in Table 4-10.

Table 4-10. Principal components analysis (PCA) to compare the 2010 data analysis (N =10) directly with the 2012 data analysis in Table 4-9 (N = 10), on the same variable basis. PCA results are also shown graphically for this 2010 comparison dataset below in Figures 4.14, 4.15, and 4.16 .

Correlation Matrix

	ClO4	Specific Cond.	NO3	SO4	Ca	Mg	Na	pH
ClO4	1.0000	0.8432	0.9695	0.9757	-0.1767	-0.0237	0.9434	0.3425
Specific Cond	0.8432	1.0000	0.7555	0.8322	0.2547	0.3449	0.9508	0.2306
NO3	0.9695	0.7555	1.0000	0.9582	-0.2432	-0.0643	0.8762	0.4911
SO4	0.9757	0.8322	0.9582	1.0000	-0.2153	-0.0423	0.9222	0.3776
Ca	-0.1767	0.2547	-0.2432	-0.2153	1.0000	0.8061	-0.0266	0.1791
Mg	-0.0237	0.3449	-0.0643	-0.0423	0.8061	1.0000	0.0815	0.2045
Na	0.9434	0.9508	0.8762	0.9222	-0.0266	0.0815	1.0000	0.1927
pH	0.3425	0.2306	0.4911	0.3776	0.1791	0.2045	0.1927	1.0000

Explained Variance (Eigenvalues)

Number	Eigenvalue	Percent	Percent	Cum Percent
1	4.7683	59.603		59.603
2	2.0138	25.173		84.776
3	0.9248	11.560		96.336
4	0.2032	2.541		98.876
5	0.0517	0.646		99.522
6	0.0308	0.385		99.907
7	0.0070	0.087		99.995
8	0.0004	0.005		100.000

Component Score Coefficients (Eigenvectors)

Variable	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
ClO4	0.45045	-0.08101	-0.03673	-0.04966	0.51378	0.10160	-0.71340	-0.05903
Specific Cond	0.41172	0.21595	-0.28548	0.19701	-0.51992	-0.10217	-0.10206	-0.61022
NO3	0.44112	-0.11232	0.16809	-0.14939	0.44547	-0.33065	0.59092	-0.29201
SO4	0.44804	-0.09769	0.00995	-0.09642	-0.16157	0.79942	0.28208	0.18859
Ca	-0.03390	0.67367	-0.06030	0.58109	0.37852	0.18036	0.15874	0.05210
Mg	0.03492	0.66052	-0.06758	-0.73986	-0.02647	-0.04198	-0.03002	0.08467
Na	0.43965	0.01183	-0.26475	0.16528	-0.17968	-0.43328	0.02945	0.69876
pH	0.19127	0.18541	0.90028	0.12139	-0.25477	-0.09384	-0.15787	0.07186

Figure 4-14. Plot showing the relationship between the primary PCs and how they account for the 2010 comparison dataset variability in the PCA evaluation shown in Table 4-10.

Figure 4-15. Loading plots showing the relationship between the primary principal components PCs (accounting for > 90% of the dataset variability) and analysis variables for the 2010 comparison dataset PCA evaluation shown in Table 4-10.
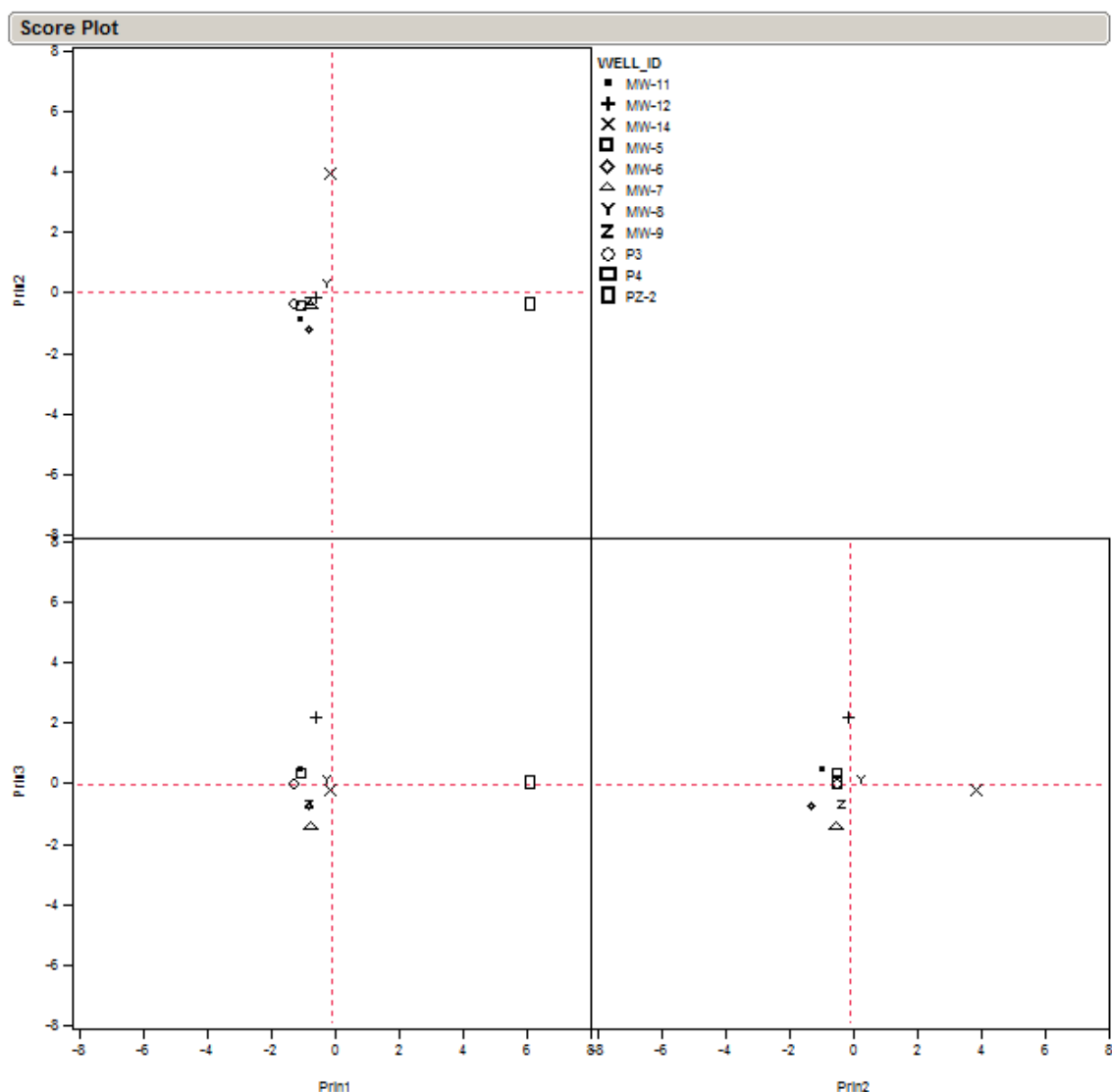
Figure 4-16. Score plots showing the relationship between the primary principal components PCs (accounting for > 90% of the dataset variability) and groundwater monitoring wells for the 2010 comparison dataset PCA evaluation shown in Table 4-10.

A comparison of the 2012 dataset PCA to the 2010 dataset PCA shows remarkable similarities, indicating that temporally and spatially consistent statistical behaviors are exhibited for the comparison variables in samples collected at sampling events 2 years apart. For forensics analysis, the dataset of choice is the more robust full 2010 dataset (N = 11, with more correlated variables) described in Table 4-6 and Figures 4-8, 4-9, and 4-10.

4.4.2 Groundwater Analyte Correlation

Correlation of perchlorate with nitrate at the Pinecastle site is consistent with a low-level natural background perchlorate signature. Through the detailed analysis of the associations between experimental variables, it is possible to ascertain if concentration gradients are significant enough to distinguish where sources might be originating. The dataset was represented primarily by two principal components, with some influence by a third principal component. PC1 and PC2 explain > 75% of the variance in the dataset, and with the addition of PC3, > 90% of the variance in the dataset is explained. The loading analysis allows clear distinctions to be made for what is driving those principal components. The following variables were positively associated with PC1, with the first four co-located: ClO_4, NO_3, SO_4, turbidity, GW elevation, pH, specific conductance, and TDS. Ca, Mg, TDS, and specific conductance were positively associated with

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PC2. GW elevation, pH, NO_3, Ca, and Mg were positively associated with PC3, with the latter two co-located. The scoring analysis indicates only one sample, PZ2, associated with a possible source of ClO_4, NO_3, SO_4, and turbidity (positive PC1), whereas MW14 was a possible source for Mg and Ca (positive PC2). Since PC3 is a relatively weak component, only explaining 15% of the total variance, a scoring analysis does not provide sufficient power for identifying strong associations. However, it appears that samples MW11, MW5, P3, PZ2, MW9, and MW6 are weakly associated with sources of NO_3, turbidity, SO_4, and ClO_4, and MW12 appears to be weakly impacted by GW elevation.

4.4.3 Relationship to Other Contaminant Studies

The GW analyte data from Pinecastle Range for both 2010 and 2012 compare reasonably well with available regional data over a 10-year period for the Ocala National Forest (USGS, 2011) as shown in Figure 4-17.
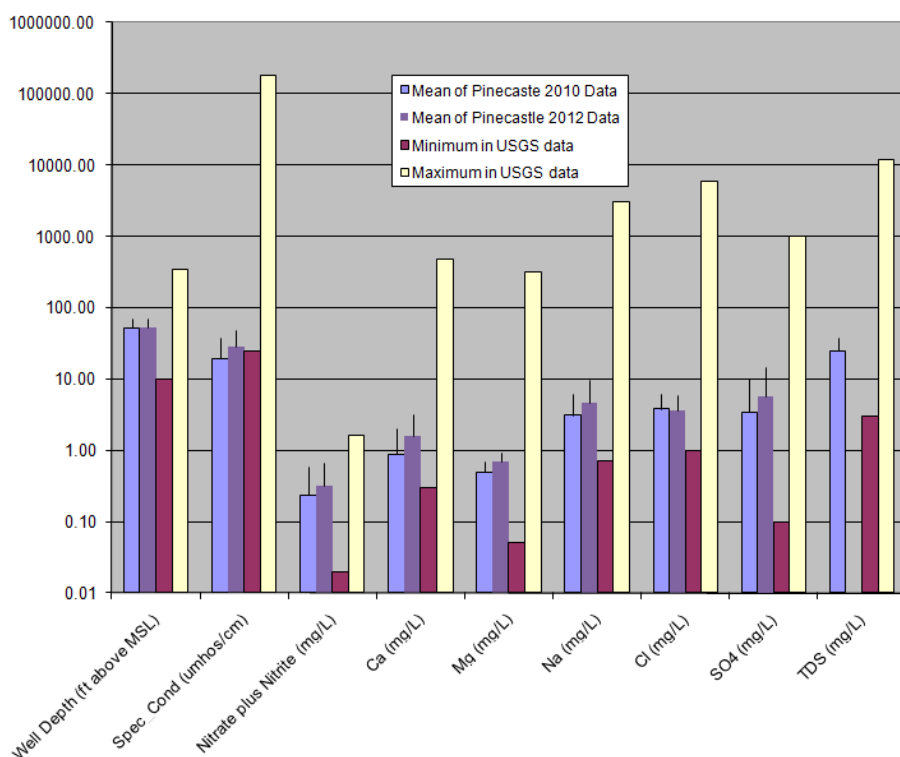

Figure 4-17. Regional GW data compared with GW data collected October 2010 and October 2012.

The observed correlation of perchlorate with nitrate in the range GW samples is consistent with previous reports of perchlorate correlations with co-occurrences of nitrate in samples collected from what the authors considered "pristine" locations across the U.S., including Florida (Parker, Serfferth, and Reese, 2008). This is illustrated in Figure 4-18 (a-b), where it is shown that nitrate levels are similar, but perchlorate levels are much lower in Range GW.

Range perchlorate values shown in Figure 4-18 (c) were quantified at a much lower detection level for correlation analysis. The level of perchlorate reported in those samples is also consistent with low levels of perchlorate observed in reference samples 2.5 km west of the range that are considered representative of regional background levels.
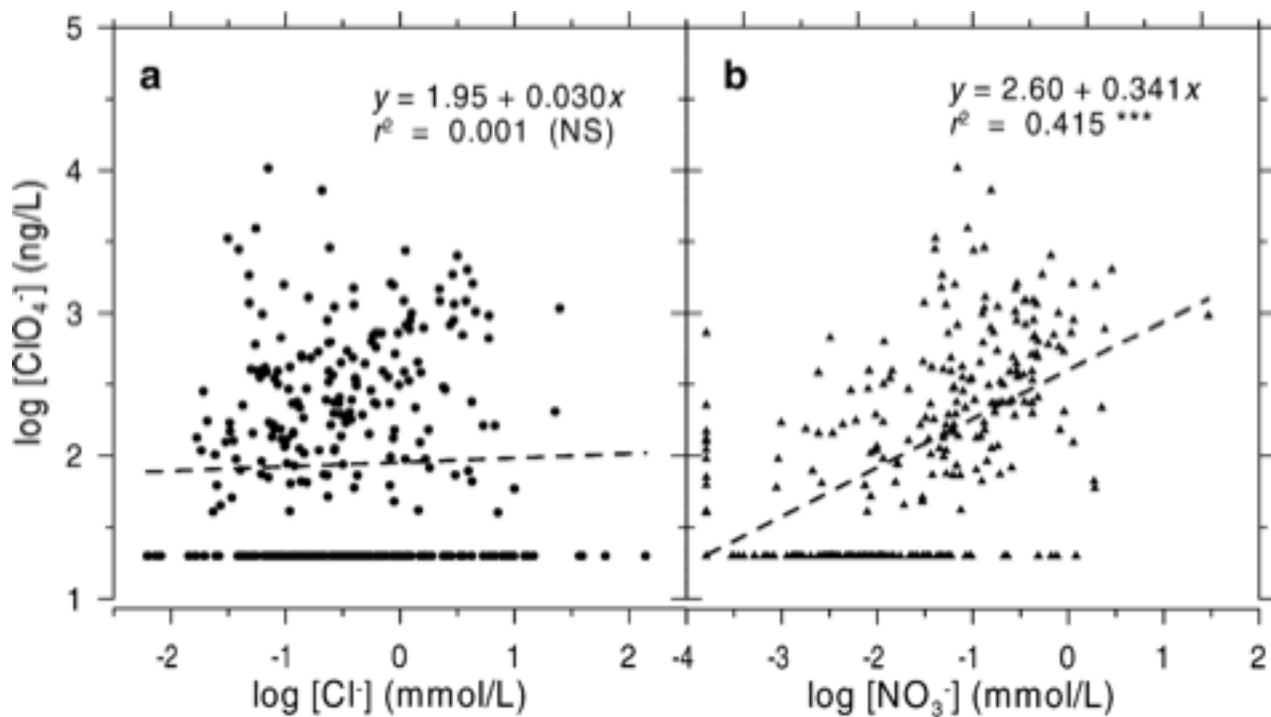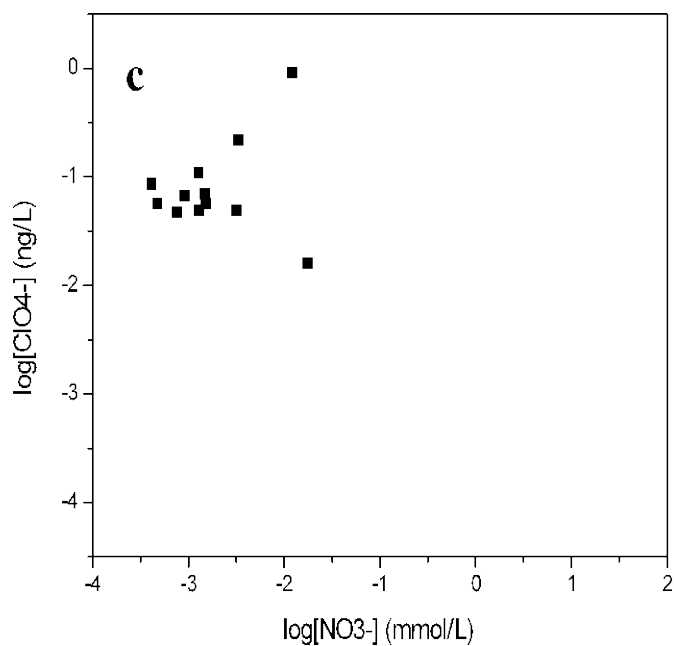
Figure 4-18. a) Chloride-perchlorate and b) nitrate -perchlorate correlation plots for "pristine" GW across the United States (Figure 4a and b reproduced from Parker, Serfferth, and Reese, 2008), and c) nitrate-perchlorate correlation plot for 2010 Range GW in this study.

4.4.4 Future Forensic Investigation Recommendations

Further forensic investigations employing isotopic analysis are not recommended for this site due to the very low levels of perchlorate in groundwater and no perchlorate signature in the range soil. Attempting to perform isotopic analyses would require a level of effort that makes it cost prohibitive, particularly for a site such as Pinecastle that does not require perchlorate mitigation. However, for a site that might be considering perchlorate remedial action, isotopic analyses could potentially be used for natural vs. synthetic source

attribution, combined with assessment of prevailing background perchlorate levels in a manner similar to described in this case study to help focus realistic cleanup targets. The forensics approach outlined in this guidance document should also be used to evaluate the need, utility, and pros/cons of potentially doing an isotopic study for a site. There have been numerous site demonstrations and guidance for using perchlorate isotopic analyses (Sturchio et al., 2007; Böhlke et al., 2005; Ader et al., 2001; Corl, 2005; Sturchio et al., 2003; Bao and Gu, 2004; Coleman, Adler, Chudhuri, and Coates, 2003; Hatzinger, Böhlke, Sturchio, and Gu, 2011; Hatzinger et al., 2009; Sturchio et al., 2006; Meier-Augenstein, 2010), which the reader is encouraged to review once a determination is made to proceed with such analyses.

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14. ABSTRACT
The objective of this document is to outline the approach, tools, and methods to quantify and distinguish the relative levels of naturally occurring perchlorate from those derived from anthropogenic sources. This will provide site managers for ranges and facilities with holistic source evaluation and identification of background perchlorate using scientifically defensible forensic approaches and methodologies. This effort brings together the current understanding of natural perchlorate characteristics and behaviors to provide a process for selecting appropriate analytical approaches developed within the environmental forensics community.

While perchlorate is not federally regulated in the natural environment, it will be facing increased regulatory pressure for future assessments and clean-up. Currently, perchlorate evaluation is part of range condition assessments and monitoring strategies per current Department of Defense (DoD) policy. Range assessments in particular have a direct impact on continued range use for training and testing/operational readiness. Quantifying natural and anthropogenic sources of perchlorate will provide an appropriate baseline for mitigating cleanup efforts and costs (above background levels). Without an understanding of the extent to which background perchlorate sources may be present at or surrounding a site and potentially impacting the site, inaccurate assessments/management decisions will result, ultimately leading to unnecessary cleanup actions at greater expense to the Navy.

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